UNITED STATES DEPARTMENT OF COMMERCE
DANIEL C. ROPER, Secretary
NATIONAL BUREAU OF STANDARDS
LYMAN J. BRIGGS, Director

✦

Journal of Research

of the

National Bureau of Standards

✦

Volume 15, Number 2
August 1935

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1935

For sale by the Superintendent of Documents, Washington, D. C. - - - - - - Price 25 cents
$2.50 per year on subscription

The prices of the separate Research Papers appearing in this JOURNAL are given on the front cover page. If 100 or more copies of any separate are ordered, a discount of 25 percent is allowed. Those who desire copies of separate Research Papers should send their orders and remittances without delay to the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. This will aid him to determine the number of copies to be printed for sale. RESEARCH PAPERS are not printed from electrotypes, and no more reprints can be had when the first and only printing is exhausted.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP815

Part of Journal of Research of the National Bureau of Standards, Volume 15, August 1935

COLOR AND SPECTRAL TRANSMITTANCE OF VEGETABLE OILS [1]

By Harry J. McNicholas [2]

ABSTRACT

A spectrophotometric analysis of 125 vegetable oils, 111 of which are from the cotton seed, has been made as a rational physical basis for the discussion and development of improved methods for the color grading of oils. The lightness and chromaticity of all the oils, and their spectral transmittance from 440 to 720 mμ, are indicated in tabular and graphical form. Consideration is given to some difficulties inherent in the color-grading problem, arising chiefly from the independent variation of the concentrations of several different pigments in the oils. Color grading in terms of the Lovibond glass standards is discussed along with other abridged methods of colorimetry suggested by the data.

CONTENTS

		Page
I.	Introduction	99
II.	Source and description of oils	100
III.	Spectral transmittance of oils	100
IV.	Colorimetric properties	106
V.	Discussion of data on oils and Lovibond glasses	113
VI.	Some abridged color-grading methods	117
VII.	Summary and conclusions	120

I. INTRODUCTION

The color of crude and refined vegetable oils is an important contributing factor in the determination of their market value. For many years the commercial color grading of these oils has been based entirely on the Lovibond system of glass standards. Many difficulties in the use of this system have arisen in practice, involving inherent properties of the system itself or as the result of the methods of application. Attempts to substitute colorimetric methods based on other material color standards have likewise failed to provide a satisfactory solution to the problem.

[1] The spectrophotometric measurements of the oils were made between July 1915 and July 1920 under the immediate supervision of I. G. Priest, with the cooperation and financial support of the Society of Cotton Products Analysts and the Interstate Cotton Seed Crushers Association. The author was employed by the above societies and detailed to the National Bureau of Standards as research associate from July 1915 to July 1916. He was then appointed to the Bureau staff. Reports involving some phases of this work have been published by Priest in the Cotton Oil Press, as follows: **3**, 86 (1919–20) no. 3; **3**, 37 (1919–20) no. 9; **4**, 95 (1920–21) no. 3.

[2] The author acknowledges the assistance of W. B. Emerson and M. K. Frehafer on some of the early spectrophotometric work. Throughout the recent analysis and preparation of data (1934–35) he is indebted to H. J. Keegan for assistance in computational work and to K. S. Gibson, D. B. Judd, and G. W. Haupt for many supplementary data supplied for the purposes of this paper. These data include all spectrophotometric or colorimetric data on the spectrum and the Lovibond glasses.

As a rational physical basis for the analysis and discussion of the problem, and for the ultimate establishment of a more desirable procedure in color grading, an extensive investigation was undertaken of the spectral-transmissive and colorimetric properties of vegetable oils, covering a wide range of color variation in cottonseed oils from different geographical sources, and a more limited range of variation in vegetable oils of different plant origin.

The present paper gives the results of this study and a discussion of some difficulties inherent in the problem. Inasmuch as the color of these oils is at present universally expressed in terms of Lovibond glasses, this color system is also extensively employed in the present paper for comparison purposes.

II. SOURCE AND DESCRIPTION OF OILS

The vegetable oils included in this investigation were generously supplied by various manufacturers, dealers, and individuals interested in the work.[3] Information is generally unavailable on details of the methods of processing, the chemical composition, and the exact geographical origin of these oils. For purely colorimetric purposes, however, it is believed that collectively they are fairly representative of the majority of the edible vegetable oils of commerce, at least of the cottonseed oils. Such oils vary in color from a light greenish yellow through canary or amber yellow to brown or deep red, and contain varying proportions of several different coloring matters commonly found in the tissues of plants.

The oils included in this work consist of 111 samples of refined cottonseed oils, designated in the tables and figures as groups A, B, D, E, and R, and 14 vegetable oils of other plant origin, herein, designated as group F. The latter group[4] includes samples of sesame, peanut, soybean, corn, rape, and olive oils. The A and B groups were received in 1915 and 1916 from 21 different refineries scattered widely throughout the country. The B group consists entirely of nearly prime wintered oils. The D group was collected in 1919 and 1920 from various individuals. The E group was obtained in 1920 through the Bureau of Chemistry and Soils of the U. S. Department of Agriculture from various sources in North Carolina, South Carolina, Georgia, Alabama, Tennessee, and Texas. The R group of refined oils was obtained in like manner along with samples of the crude oils from which the refinings were made.

III. SPECTRAL TRANSMITTANCE OF OILS

Complete information on the color of an oil may be derived when the transmission of light is specified for the oil at various wave lengths throughout the visible spectrum. Such measurements have been made for a 5¼ inch thickness of each oil and the results represented graphically by the curves in figures 1 to 5. In these figures the solid-line curves represent cottonseed oils and the broken-line

[3] The donors include Armour and Co., Harris Abattoir (Toronto), Procter and Gamble, Peet Bros., Globe Soap Co., Refuge Cotton Oil Co., Swift and Co., The Fort Worth Laboratories, Southern Cotton Oil Co., Corn Products Co., Phoenix Cotton Oil Co., Portsmouth Cotton Oil Co., Gunns Limited (Toronto), Capitol Refining Co., Armstrong Packing Co., Trinity Cotton Oil Co., American Cotton Oil Co., Falkenburg and Co., Empire Cotton Oil Co., Temple Cotton Oil Co., Independent Cotton Oil Co., Sea Island Cotton Oil Co., Magic City Oil Co., Felix Paquin, T. C. Law, F. N. Smalley, David Wesson, and P. S. Tilson.

[4] Spectrophotometric data for oils F 10 to F 14 were taken from the work of Wesson, Cotton Oil Press 6, no. 5 (September 1922).

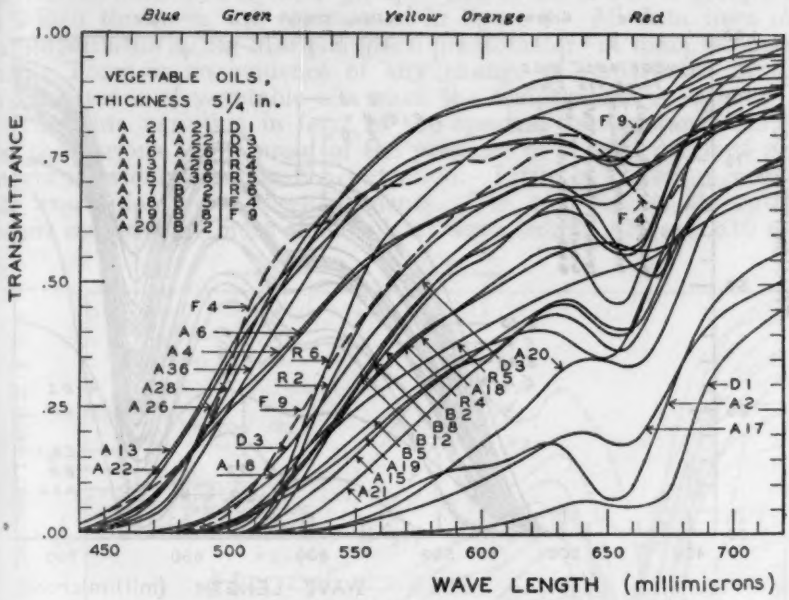

FIGURE 1.—*Spectral transmittance of vegetable oils.*
[Thickness 5¼ inches]

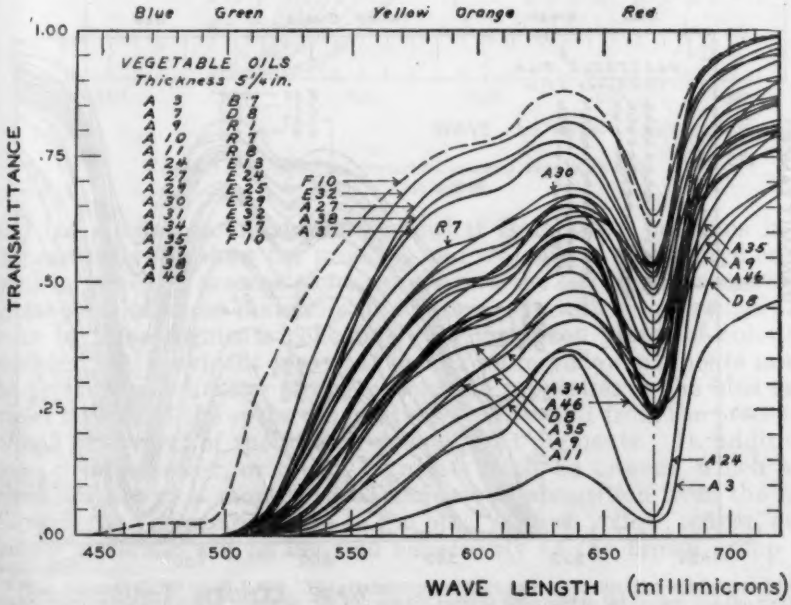

FIGURE 2.—*Spectral transmittance of vegetable oils.*
[Thickness 5¼ inches]

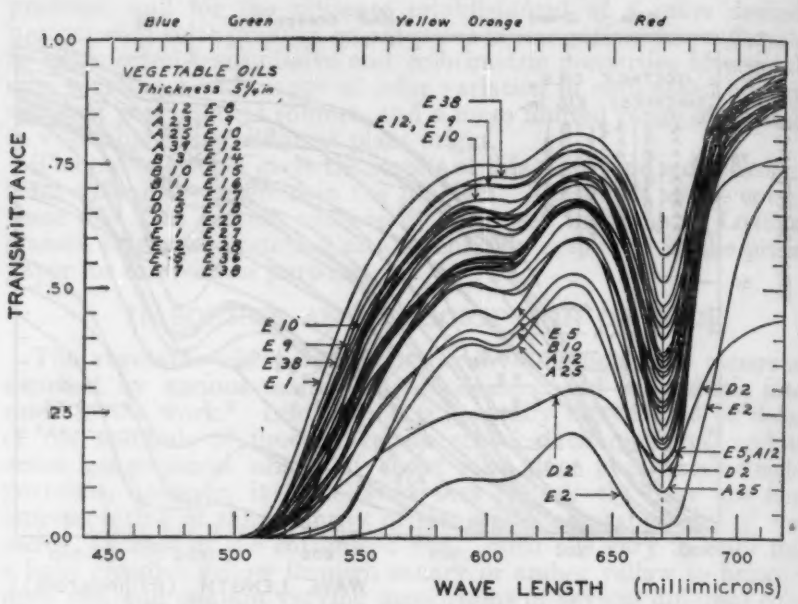

FIGURE 3.—*Spectral transmittance of vegetable oils.*
[Thickness 5¼ inches]

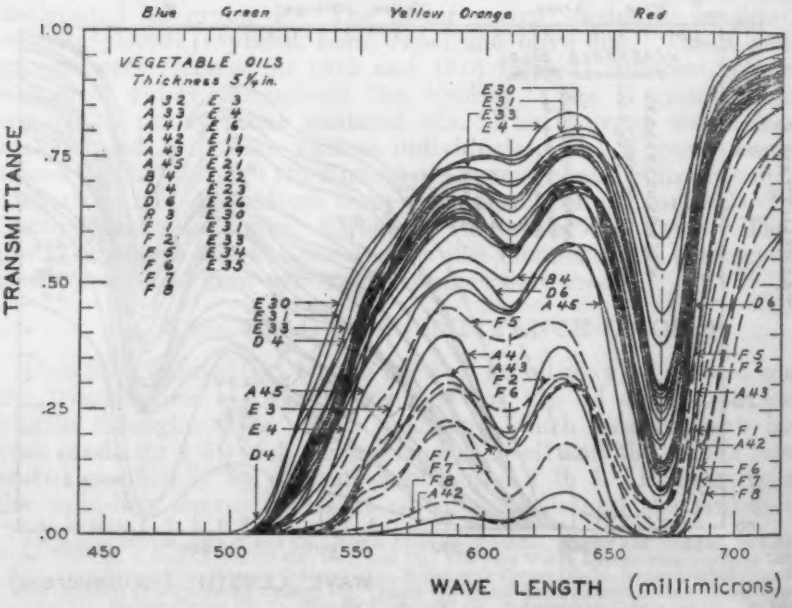

FIGURE 4.—*Spectral transmittance of vegetable oils.*
[Thickness 5¼ inches]

curves the other oils of the F group. Oils of the A and B groups, in a ⅜ inch thickness, are represented in figure 6. All data were obtained with the König-Martens spectrophotometer [5] at room temperature. There is no evidence of any change of importance in the transmittance of vegetable oils when the temperature is varied.[6]

The wide variation in form of the spectral-transmittance curves for the various oils is proof of the presence of several different pigments in widely varying concentration. Little is known regarding the exact identity of these pigments. The well-defined absorption bands centered for most of the oils at wave lengths 670 and 610 mμ,

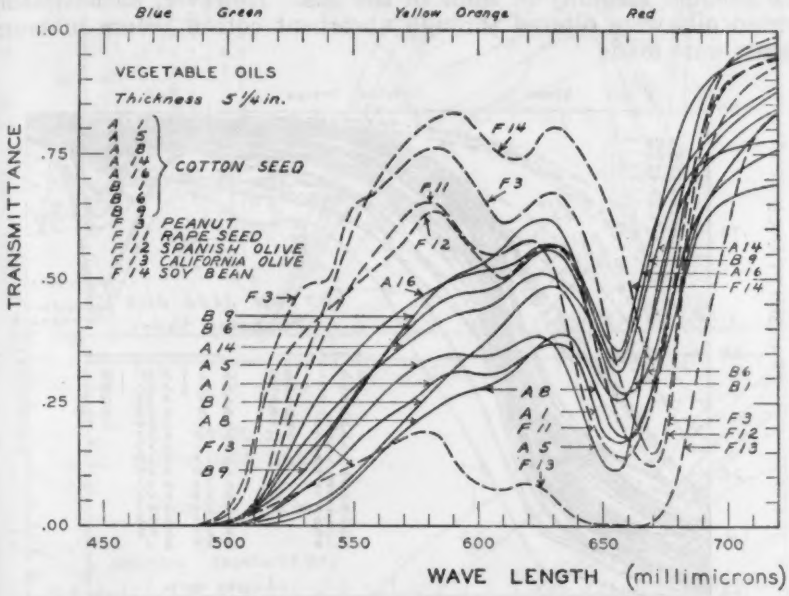

FIGURE 5.—*Spectral transmittance of vegetable oils.*
[Thickness 5¼ inches]

and the similar bands shifted somewhat from these positions in a few cases (fig. 5), show the presence undoubtedly of chlorophyll compounds, which, if present alone, would give the oils the characteristic green color of these materials in solution. It will be convenient to refer to these pigments collectively as the green group of coloring matters. It is evident also that one or more yellow pigments must be present, which have strong absorptive properties in the blue and violet regions of the spectrum, such as would result from the presence of one or several of the known yellow plant pigments. In addition some yellow, amber, or brown pigments must be present, which are characterized by a more gradual increase in absorption from the red through the yellow and green to the blue. These yellow, amber, and brown materials will be denoted collectively as the brown group of

[5] BS J. Research **1**, 793 (1928) RP30. The arrangement of light source and auxiliary equipment for th spectrophotometric analysis of vegetable oils was not the same as described in this paper, but the method of measurement was essentially the same. Brass cells with glass end-plates were used to contain the oils The measured transmission of these end-plates with a thin film of bleached oil between was found to be 0.892 for all wave lengths. Each measured transmission value of the cell filled with oil was divided by this number to give the transmittance of the oil itself as represented in the figures and in table 1.

[6] See Judd, BS J. Research **1**, 859, footnote 18, (1928) RP31.

pigments and are of considerable importance in determining the color of the oil in a 5¼ inch thickness. The general trend of the spectral-transmissive properties for the brown group is represented by those curves in figures 1 and 7 which exhibit little trace of the chlorophyll bands. Figure 7, lower part, shows the spectral transmittance of some crude cottonseed oils, herein denoted as the C group. During refining the brown pigments are removed in greater proportion than the green, as illustrated particularly by the transition from C 3 to R 3. Another factor possibly affecting the transmittance curves is the nearly nonselective scattering of light introduced by the residual turbidity of some of the oils. However, all noticeably turbid oils were filtered through absorbent cotton before measurements were made.

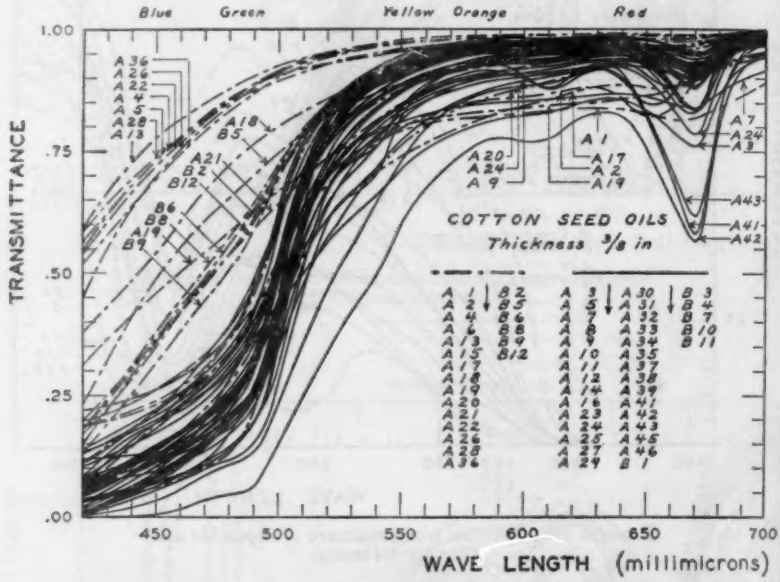

FIGURE 6.—*Spectral transmittance of cottonseed oils.*
[Thickness ⅜ inch]

In figures 1 to 4 the oils have been roughly classified in accordance with the form of their transmittance curves. All the oils show a strong absorption in the violet and blue regions of the spectrum, which increases markedly with increasing yellowness or redness of the oils. Through the color transition we observe the existence of two principal spectral types. The "green" type (fig. 4) is characterized by the presence chiefly of the green group of pigments with their sharp bands in the orange and red and lesser bands usually accompanying a sharp decrease in transmittance from the yellow into the green. The "brown" type (fig. 1), on the other hand, shows no very pronounced absorption bands and exhibits a more gradual decrease in transmittance through the yellow and green. The two types of oils are observed to merge one into the other so that the observed color variations in a 5¼ inch thickness may be ascribed to a corresponding variation in the absolute and relative concentrations of the two groups of pigments. It is probable that for purely colori-

metric purposes the color variation over the entire range of vegetable oils could be satisfactorily described in terms of the independent

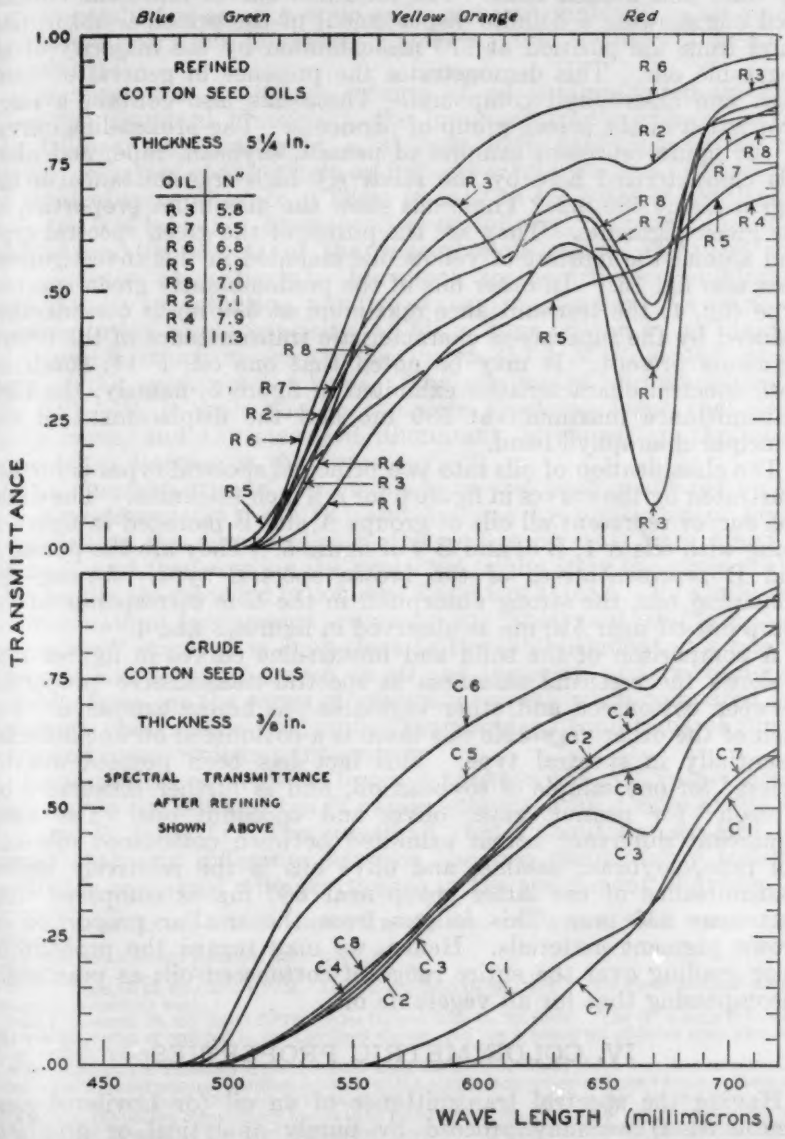

FIGURE 7.—*Spectral transmittance of crude cottonseed oils and refinings from same.*

Showing the effect of the refining process on the selective removal of pigment components in the oils, and the reduction in total pigment content. The thickness ratio of crude to refined oils, found necessary to obtain comparable transmittance data, shows (by Beer's law) that the reduction in total pigment content is roughly 93 percent.

variation in concentration of two hypothetical pigments representative of the brown and green groups, respectively. This point is further discussed in section VI.

In figure 5 two small groups of oils are shown, each differing slightly from the oils in the preceding figures, and represented, respectively, by solid and broken lines. The solid-line curves represent cottonseed oils showing a definite displacement of the principal absorption band from the position at 670 mμ exhibited by the majority of all vegetable oils. This demonstrates the presence in general of more than one chlorophyll compound. These oils also contain a large proportion of the brown group of pigments. The broken-line curves in the figure represent samples of peanut, soybean, rape, and olive oils characterized here by the relatively high transmittance in the region about 580 mμ. These oils show the maximum proportion of the green pigments. They are the purest of the green spectral type and among the lightest of yellow oils included in this investigation. (See also fig. 10.) In other oils of the predominantly green spectral type (fig. 4) the transmittance maximum at 580 mμ is considerably reduced by the superposed characteristic transmittance of the brown pigments present. It may be noted that one oil, F 11, combines both spectral characteristics exhibited in figure 5, namely, the high transmittance maximum at 580 mμ and the displacement of the principal chlorophyll band.

The classification of oils into two principal spectral types is further illustrated by the curves in figure 6 for a ¾ inch thickness. The dash-dot curves represent all oils of groups A and B included in figure 1, along with oils A 1, B 6, and B 9 of figure 5. They are the purest A and B representatives of the brown spectral type. Among the remaining oils, the strong absorption in the blue corresponds to the sharp cut-off near 510 mμ as observed in figures 3 and 4.

A comparison of the solid and broken-line curves in figures 1 to 5 shows the essential sameness in spectral-transmissive properties between cottonseed and other vegetable oils herein examined. For each of the other vegetable oils there is a cottonseed oil not differing essentially in spectral type. This fact has been pointed out by Priest [7] for one sample of soybean oil, and is further illustrated by Wesson [8] for peanut, rape, olive, and cocoanut oils. The most significant difference herein exhibited between cottonseed oils and the rape, soybean, sesame, and olive oils is the relatively higher transmittance of the latter group near 580 mμ as compared with that near 630 mμ. This follows from the smaller proportion of brown pigment materials. Hence, we may regard the problem of color grading over the entire range of cottonseed oils as practically encompassing that for all vegetable oils.

IV. COLORIMETRIC PROPERTIES

Having the spectral transmittance of an oil (or Lovibond-glass combination) we may proceed by purely analytical or graphical methods to derive [9] various desired colorimetric specifications, with reference to a standard illuminant, observer, and coordinate system. In the present paper the standard illuminant is Abbot-Priest sun,[10]

[7] Cotton Oil Press (January 1920).
[8] Cotton Oil Press 6, no. 5 (September 1922). These spectrophotometric data on the peanut, rape, and olive oils are reproduced in the present paper.
[9] For methods of computing colorimetric properties from spectral transmittance and other data, see J. Opt. Soc. Am. and Rev. Sci. Instr. 6, 527 (1922); J. Opt. Soc. Am. 23, 359 (1933).
[10] J. Opt. Soc. Am. and Rev. Sci. Instr. 12, 479 (1926).

which serves also as the basic stimulus [11] for a trilinear coordinate system.[12] The standard observer and coordinate system are defined by the (extrapolated) OSA visual response functions.[13] These reference conditions are the same as have been employed in all standardization work on Lovibond glasses at the National Bureau of Standards.[14]

Assuming that a 5¼-inch column of oil is illuminated by light from the standard illuminant, the luminous transmittance T, and the trilinear coordinates (r, g, b) have been determined from the given properties of the source and observer and the measured values of spectral transmittance. These quantities are listed in columns 3, 4, 5, and 6 of table 1. They specify, respectively, the purely luminous and chromatic aspects of the vegetable-oil colors (lightness and chromaticity, respectively). Inasmuch as the trilinear coordinates sum to unity by definition, any two of them may be used in a graphical representation of chromaticity. This is done on the (r, g) diagram of figure 8, which shows the Lovibond 35Y+N''R locus [15] and a part of the spectrum (λ) locus. The relation of chromaticities on the 35Y+N''R scale to the complete spectrum locus, the blackbody locus, and the standard illuminant, is shown on the small-scale (r, g) diagram in the figure.

The chromaticities of all the oils have also been evaluated on the one-dimensional (35Y+N''R) and λ scales by projection of points representing the oils parallel to the system of cross lines drawn in figure 8, and then reading the projected points from the given scales. The results are recorded in columns 8 and 9 of table 1. To a sufficient approximation for present purposes the analytical and graphical procedure [16] involved is equivalent to the establishment of a nearest chromaticity setting between an oil and the series of Lovibond-glass combinations (or the series of spectrum colors), when compared in a two-part photometric field under the standard conditions of illuminant and observer herein prescribed.

A comparison is made in figure 9 between the N'' values herein assigned to the oils and the N values submitted by donors of the oils (column 7, table 1). The spread of values about the straight line shows that any difference between the two chromaticity scales is negligible compared with erraticisms in the assignment of grades.

[11] J. Guild, *On the fixed points of a colormetric system, Discussion by Priest,* Trans. Opt. Soc. **32,** 25 (1930-31).

[12] J. Opt. Soc. Am. and Rev. Sci. Instr. **9,** 506 (1924).

[13] J. Opt. Soc. Am. and Rev. Sci. Instr. **10,** 230 (1925).

[14] BS J. Research **13,** 433 (1934) RP718. Also Oil and Soap **11,** 246 (1934). This paper contains complete references to previous work.

[15] BS J. Research **13,** 433 (1934) RP718. Also Oil and Soap **11,** 246 (1934). The N''R scale is based on the new derivation of unit red in the Lovibond system, yielding a consistent additive scale when combined with 35 yellow.

[16] To determine the directions of the projection lines, the 35Y+$N''\lambda$ and N loci were first transferred by a prescribed transformation of coordinates from the OSA colorimetric system of figure 8 to the uniform-scale system devised by Judd, J. Research NBS **14,** 41 (1935) RP756; or J. Opt. Soc. Am. **25,** 24 (1935). In this new system, the nearest chromaticity match to be found for a given color out of any series of colors (such as the 35Y+N''R series, or the series of spectrum colors) is determined by drawing the shortest line (the perpendicular) from the point representing the given color to the locus representing the series. Accordingly, sets of perpendiculars were drawn both to the 35Y+N''R locus and to the spectrum locus; but since these loci in the uniform-scale system are nearly straight, parallel lines, these sets of perpendiculars are almost identical. Hence, one set will serve to determine both N'' and λ values of any color represented by points in the neighborhood of these loci. The series of cross lines shown in figure 8 corresponds to this set of perpendiculars.

The luminous transmissions [17] of the cell-plus-oil and Lovibond-glass combinations are compared in the upper part of figure 8. Values for combinations of 2, 3, and 4 glasses are shown.

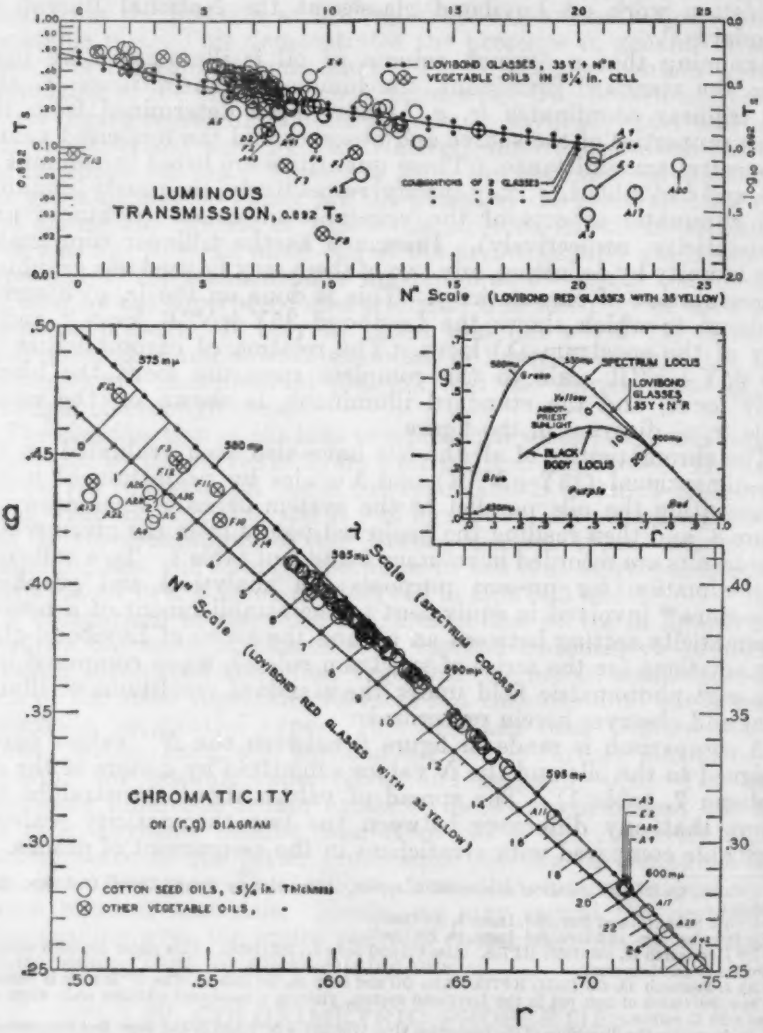

FIG. 8.—*Colorimetric properties of vegetable oils.*

In figures 10 to 16 the spectral-transmittance curves for all the oils are replotted in a new classification, this time in accordance with their color grade. Again solid lines represent cottonseed oils and broken lines the other vegetable oils. The filled circles show the

[17] Luminous transmissions differ from the luminous transmittances in column 3 of table 1 by a factor 0.892, as explained in footnote 5. Luminous transmissions given in figure 8 for a combination of two Lovibond glasses are multiplied by 0.901 and $(0.901)^2$, respectively, to obtain the transmissions for a combination of 3 or 4 glasses. Multiple reflections between glass surfaces are disregarded. The number 0.901 is the transmission of a single clear glass.

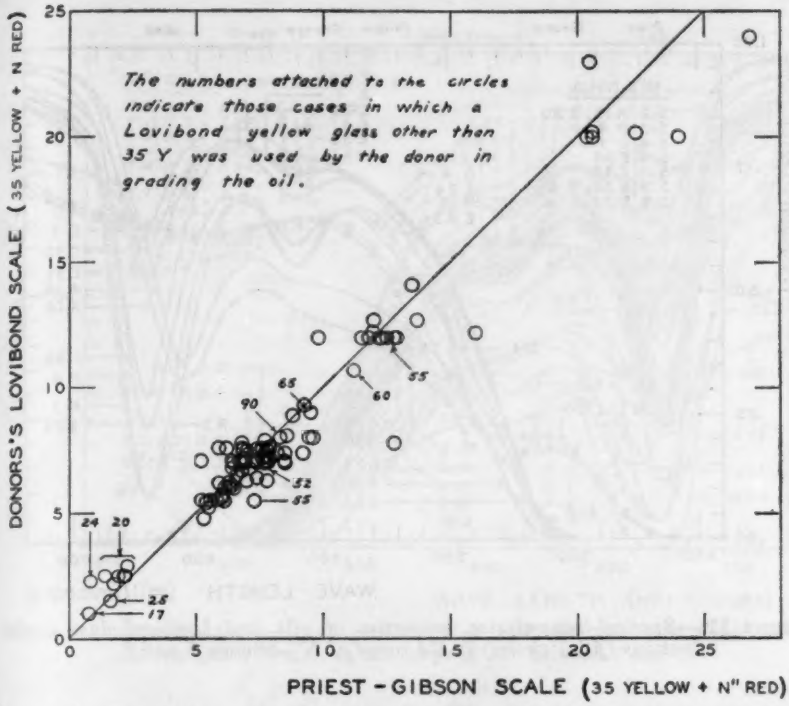

FIGURE 9.—*Comparison of Lovibond grades assigned by donors of oils with those derived in the present investigation.*

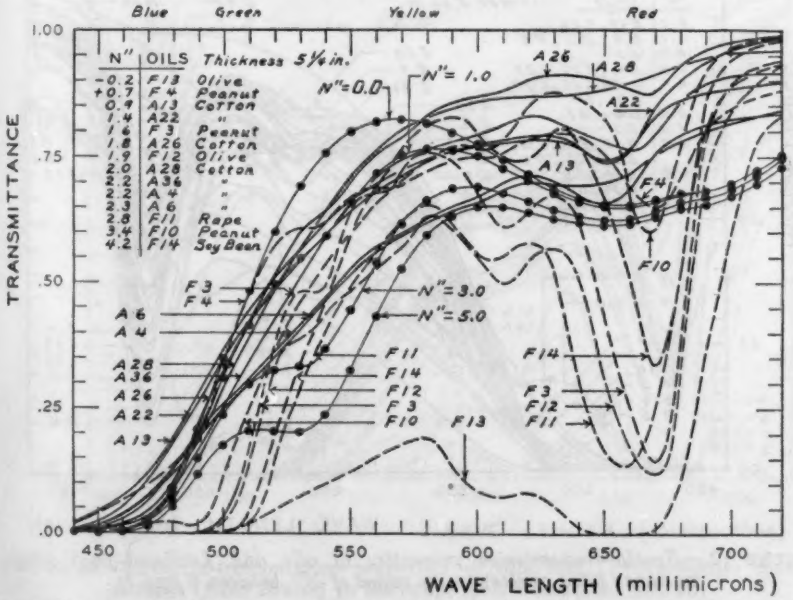

FIGURE 10.—*Spectral-transmissive properties of oils and Lovibond-glass combinations (filled circles) in the range of N" between 0 and 5*

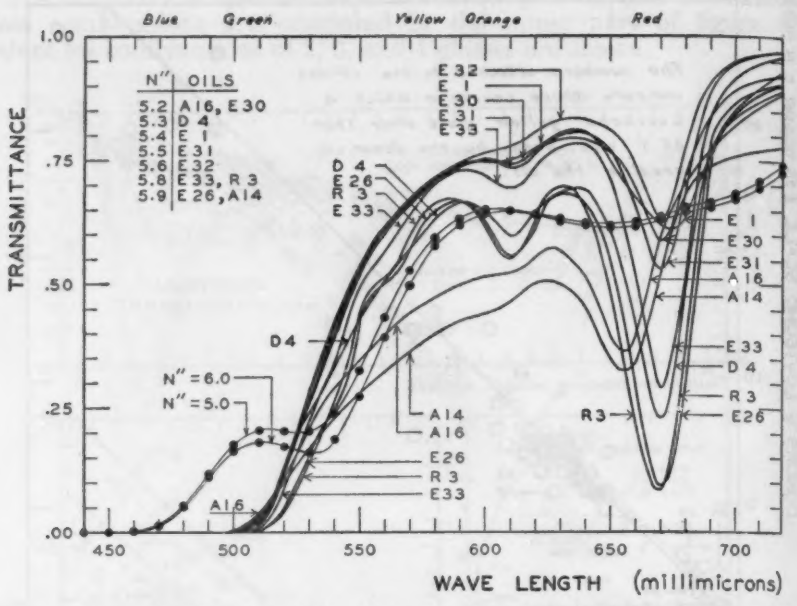

FIGURE 11.—*Spectral-transmissive properties of oils and Lovibond-glass combinations (filled circles) in the range of N" between 5 and 6*

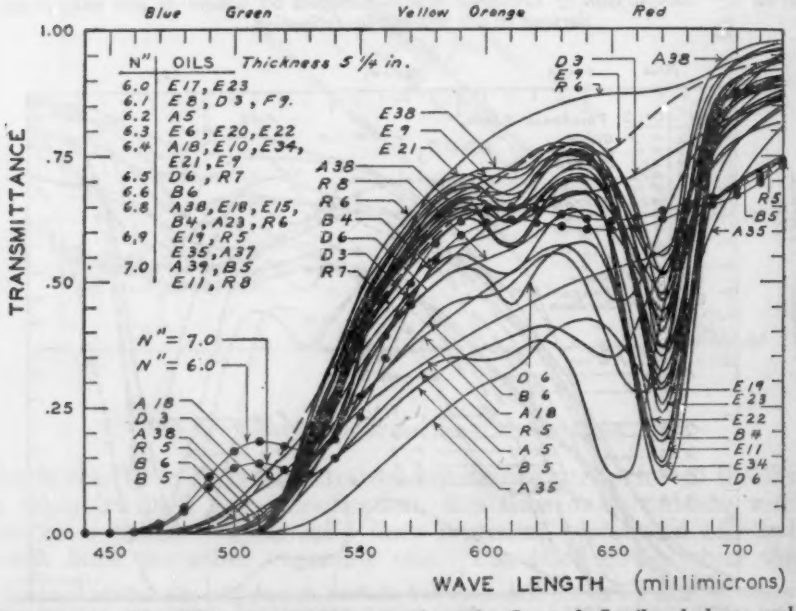

FIGURE 12.—*Special-transmissive properties of oils and Lovibond-glass combinations (filled circles) in the range of N" between 6 and 7*

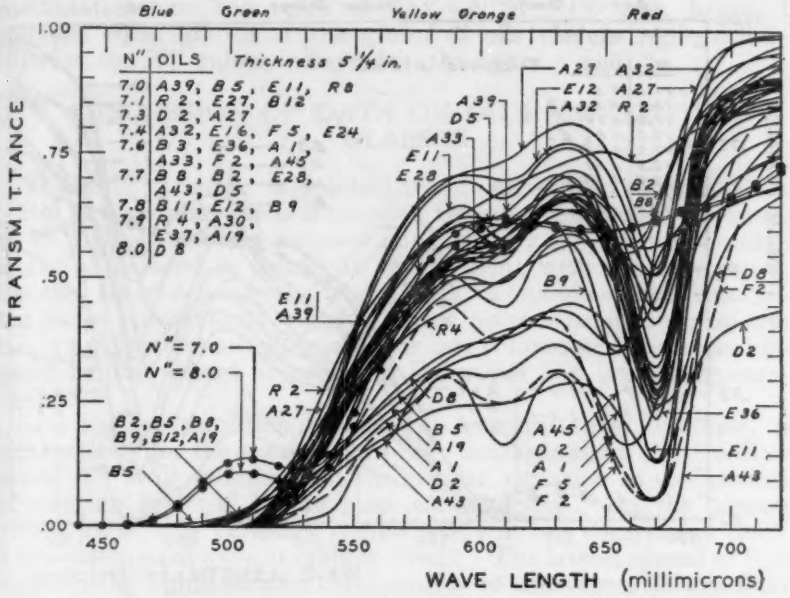

FIGURE 13.—*Spectral-transmissive properties of oils and Lovibond-glass combinations (filled circles) in the range of N" between 7 and 8.*

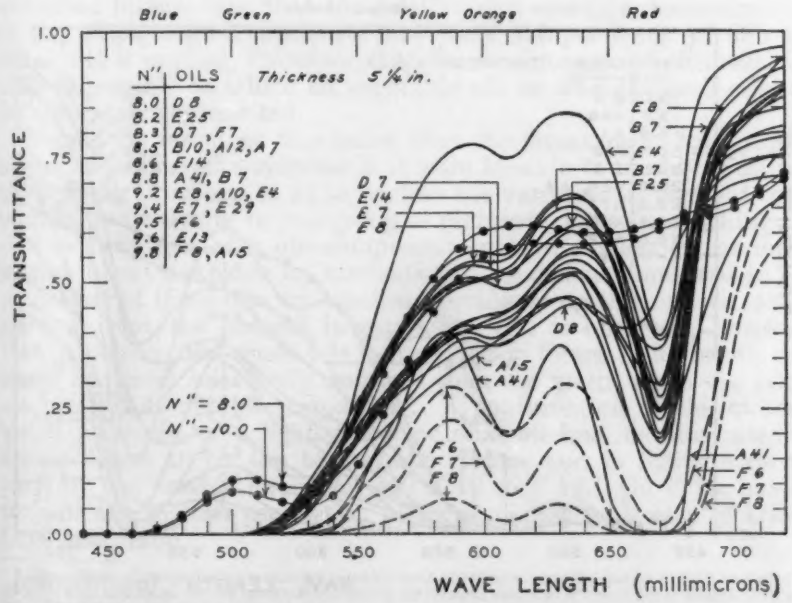

FIGURE 14.—*Spectral-transmissive properties of oils and Lovibond-glass combinations (filled circles) in the range of N" between 8 and 10.*

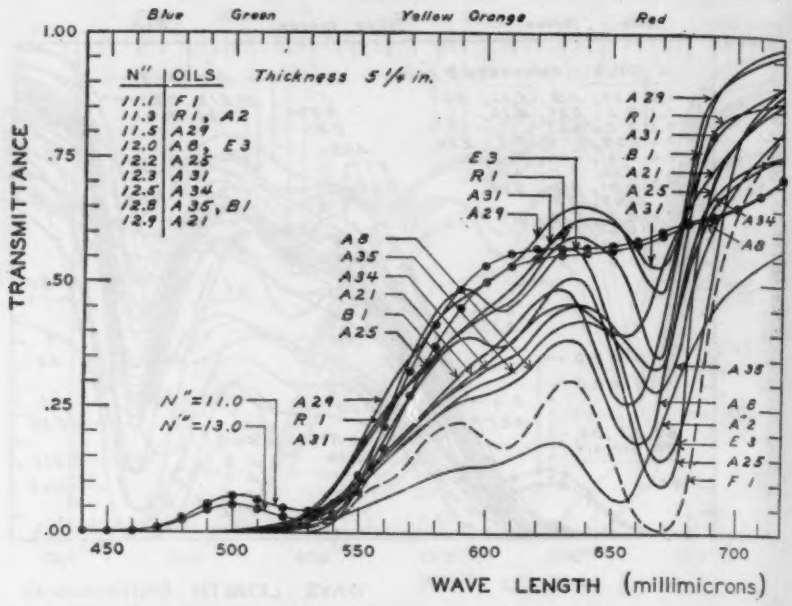

FIGURE 15.—*Spectral-transmissive properties of oils and Lovibond-glass combinations (filled circles) in the range of N" between 11 and 13.*

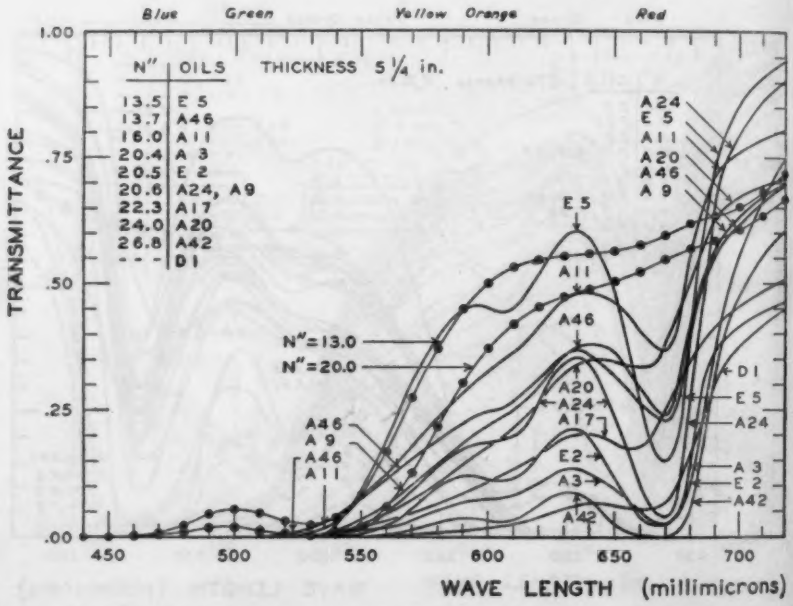

FIGURE 16.—*Spectral-transmissive properties of oils and Lovibond-glass combinations (filled circles) in the range of N" between 13 and 20.*

course of the spectral-transmittance [18] curves for Lovibond-glass combinations on the scale of $35Y+N''R$. In each figure, the assigned color grades of the group of oils therein represented lie between the N'' values indicated in the figure.

V. DISCUSSION OF DATA ON OILS AND LOVIBOND GLASSES

The wide variation in spectral-transmissive properties within the group of vegetable oils is illustrated by the classification in figures 1 to 5. A like variation between oils of nearly the same chromaticity is also illustrated in figures 10 to 16, along with the divergence of the oils, taken collectively, from the Lovibond-glass combinations in the same chromaticity range. These variations in spectral-transmissive properties are all translated into colorimetric terms and indicated by the spread of points in the upper and lower diagrams of figure 8.

The regular variation in spectral transmittance, lightness, and chromaticity for the sequence of color standards along the one-dimensional N'' scale follows from the regular variation in concentration of coloring material in the glass combinations. On the constant-yellow basis, this variation resides solely in one component (red) of a two-component system (yellow+red). The lateral spread of points representing lightness and chromaticity of the vegetable oils follows from the irregular variations in form of the spectral-transmittance curves, and, assuming for simplicity that these variations may be ascribed likewise to variations in a two-component system (hypothetical brown and green pigments), we find the important difference exhibited in this case that the relative and absolute concentrations of the oil-pigment components may vary independently of one another. It is implied, therefore, that no one-dimensional chromaticity scale is possible on which all vegetable oils or all cottonseed oils can be accurately represented.

It may be noted at this point that the situation in this respect might be improved somewhat if it were feasible to modify or control the refining processes so as to confine the variation in pigment composition more nearly to one group of pigments, thus approaching the simpler condition of a one-component system. Inasmuch as information is not available on methods and conditions employed in the processing of these oils, no conclusive evidence on this matter can be gleaned from the present investigation. It is observed, however, that in refining the crude oils represented in figure 7 the brown pigments are more selectively removed than the green, when the latter are present in notable proportion. A continuation of this process would yield oils of a light-yellow or olive-oil hue, as illustrated in figures 5 and 10 by the broken-line curves, and in figure 8 (lower part) by the crossed circles for oils F 10 to F 14. Oil F 13, having perhaps the highest proportion of green pigments, is also of lowest Lovibond grade.

[18] Given spectral-transmission curves for combinations of 2 glasses were divided by $(0.901)^3$ to derive the values of transmittance. When transmission curves for integral values of N'' were not available, they were found for present purposes by interpolation.

It is known that the green pigments are the most fugitive to the bleaching action of light and chemical agents. Wesson [19] has shown for two samples of cottonseed oils that the bands at 670 and 610 mμ are nearly completely removed by the treatment with fuller's earth, and unpublished experiments of the author show the same effect after exposure to sunlight. When the brown pigments are present in considerable proportion, the removal of the green pigments does not have a large effect on the color. The absence of the green pigments would tend to confine the observed variation in chromaticity more closely to a one-dimensional range determined solely by the varying concentration of the brown pigments.

The fixed amount of yellow coloring material used in the combination of 35Y+N''R leads to the fact illustrated in figure 8 that none of the oils included in this investigation fall exactly on the established N'' scale, hence, none of these oils are accurately matched in chromaticity by any possible combination of a fixed 35-yellow with variable red. The position of the locus of glass combinations could be brought more nearly into coincidence with the general trend of points for the vegetable oils by use of a glass of yellow numeral higher than 35. This was corroborated by some experimental work with the B group of cottonseed oils. A color comparator was used, provided with means for equalizing brightnesses, and the chromaticities of the oils and Lovibond glasses were matched as closely as possible first with 35-yellow and variable red. Then, with the red value kept constant, more yellow was added until the best chromaticity match was obtained. It was found on the average that 80-yellow was required for these oils. This shift in the locus of glass combinations would be less suitable, however, for very light cottonseed oils; for, as recorded in table 1 and figure 9, the oils between N'' values of 1 and 3 were graded experimentally on a low-yellow basis in the neighborhood of 20Y.

It is evident that an improved one-dimensional Lovibond scale, which would coincide with the general trend of points for all vegetable oils, would require a fixation of the yellow numeral in some functional relation to the red. For the most accurate color grading, however, a two-dimensional Lovibond scale, with independent variation of both yellow and red, is necessary to cope completely with the independent variation in pigment concentrations within the group of vegetable oils.

A comparison of the luminous transmissions of the oils and Lovibond glasses in the upper part of figure 8 shows a general agreement in lightness, but the spread of the oils in this respect is greater than can be matched by any convenient choice of the number of clear and colored glasses used in the combination while maintaining the best chromaticity match. This condition introduces serious uncertainties in the present practice of color grading, because of the residual brightness difference between the fields of the color comparator when the final chromaticity setting is made.

It is evident from the data herein presented that the accurate color grading of vegetable oils can be based only on a two-dimensional chromaticity scale, which must be embodied in a colorimeter provided also with means for the independent equalization of brightnesses in the sample and comparison fields. Many such two-dimensional

[19] Cotton Oil Press 6, no. 5 (September 1922).

scales could be devised and employed, provided there is no objection to the added complication in color grading. For limited ranges of color variation it is sometimes satisfactory for practical purposes to fix one of the scale variables at a constant value, or restrain its variation in some fixed relation to the other dimension, so that a one-dimensional scale is effectively established. Illustrations of these possibilities have been given for the Lovibond system of yellow and red glasses and further examples are discussed in the following section.

TABLE 1.—*Colorimetric properties of vegetable oils for a thickness of 5¼ inches*

NBS lab. no.	Kind of oil or source	Sunlight transmittance	Trilinear coordinates			Lovibond grade			Wave length	Spectral transmittance shown in	
						By donor		By NBS on 35Y basis			
		T_s	r	g	b	Y	R	R	λ	Figure	Figure
1	2	3	4	5	6	7		8	9	10	11
A1		0.183	0.6093	0.3822	0.0085	35	7.6	7.6	587.0	5	13
A2		.070	.6477	.3461	.0062	35	12.0	11.3	591.3	1	15
A3		.034	.7140	.2832	.0028	35	20.0	20.4	599.5	2	16
A4		.521	.5262	.4260	.0477	20	2.5	2.2	579.8	1	10
A5		.213	.5934	.3976	.0090	35	7.6	6.2	585.3	5	12
A6		.514	.5255	.4236	.0509	20	2.9	2.3	579.9	1	10
A7		.249	.6195	.3726	.0079	35	7.4	8.5	588.1	2	14
A8		.142	.6540	.3409	.0051	35	12.2	12.0	592.0	5	15
A9		.098	.7153	.2818	.0029	35	20.2	20.6	599.7	2	16
A10		.234	.6269	.3659	.0072	35	7.4	9.2	588.9	2	14
A11		.154	.6863	.3098	.0040	35	12.2	16.0	596.1	2	16
A12		.227	.6200	.3736	.0064	35	7.0	8.5	588.1	3	14
A13		.640	.5002	.4339	.0659	24	2.3	0.9	578.3	1	10
A14		.286	.5894	.3996	.0110	35	7.6	5.9	585.0	5	11
A15		.203	.6330	.3596	.0075	35	12.0	9.8	589.6	1	14
A16		.338	.5809	.4078	.0113	35	7.1	5.2	584.1	5	11
A17		.504	.7233	.2736	.0032	35	20.2	22.3	600.7	1	16
A18		.305	.5919	.3928	.0153	35	7.1	6.4	585.5	1	12
A19		.213	.6116	.3771	.0113	35	7.6	7.9	587.5	1	13
A20		.082	.7314	.2657	.0029	35	20.0	24.0	601.7	1	16
A21	Refined cottonseed oils, received June 1915 from various manufacturers	.170	.6612	.3326	.0062	35	12.0	12.9	592.9	1	15
A22		.629	.5108	.4314	.0578	20	2.5	1.4	578.3	1	10
A23		.404	.6010	.3908	.0083	35	7.8	6.8	586.1	3	12
A24		.084	.7151	.2821	.0028	35	20.0	20.6	599.7	2	16
A25		.188	.6569	.3388	.0043	35	12.0	12.2	592.3	3	15
A26		.690	.5244	.4351	.0405	20	2.2	1.8	579.0	1	10
A27		.434	.6065	.3855	.0080	35	7.1	7.3	586.7	2	13
A28		.682	.5246	.4313	.0441	20	2.5	2.0	579.3	1	10
A29		.262	.6496	.3449	.0055	35	12.0	11.5	591.5	2	15
A30		.346	.6128	.3789	.0083	35	7.2	7.9	587.4	2	13
A31		.234	.6568	.3379	.0053	35	12.0	12.3	592.3	2	15
A32		.405	.6075	.3852	.0073	35	7.6	7.4	586.8	4	13
A33		.352	.6100	.3827	.0073	35	7.6	7.6	587.0	4	13
A34		.166	.6583	.3362	.0055	35	12.0	12.5	592.5	2	15
A35		.151	.6609	.3337	.0054	55	12.0	12.8	592.8	2	15
A36		.624	.5320	.4323	.0358	20	2.5	2.2	579.7	1	10
A37		.417	.6023	.3892	.0085	35	7.1	6.9	586.3	2	12
A38		.437	.5999	.3912	.0089	35	7.1	6.8	586.0	2	12
A39		.378	.6024	.3893	.0083	35	7.1	7.0	586.3	3	12, 13
A41		.158	.6238	.3716	.0046	35	8.9	8.8	588.4	4	14
A42		.118	.7448	.2531	.0021	35	24.0	26.8	603.2	4	16
A43		.139	.6124	.3821	.0055	35	7.9	7.7	587.2	4	13
A45		.279	.6107	.3825	.0068	35	7.6	7.6	587.1	4	13
A46		.123	.6687	.3263	.0050	35	12.7	13.7	593.8	2	16

TABLE 1.—*Colorimetric properties of vegetable oils for a thickness of 5¼ inches*—Continued

NBS lab. no.	Kind of oil or source	Sunlight transmittance	Trilinear coordinates			Lovibond grade			Wave length	Spectral transmittance shown in	
						By donor		By NBS on 35Y basis			
		T_s	r	g	b	Y	R	R	λ	Figure	Figure
1	2	3	4	5	6	7		8	9	10	11
B1	Prime winter cottonseed oils	0.175	0.6609	0.3334	0.0057	35	7.8	12.8	592.9	5	15
B2		.325	.6100	.3803	.0097	35	7.0	7.7	587.2	1	13
B3		.324	.6094	.3827	.0079	35	7.2	7.6	587.0	3	13
B4		.330	.6004	.3913	.0084	35	6.7	6.8	586.1	4	12
B5		.225	.5999	.3871	.0131	35	6.3	7.0	586.3	1	12
B6		.289	.5976	.3921	.0104	35	6.5	6.6	585.9	5	12, 13
B7		.292	.6232	.3698	.0070	45	7.2	8.8	588.5	2	14
B8		.337	.6096	.3805	.0099	35	7.0	7.7	587.2	1	13
B9		.301	.6118	.3792	.0090	35	6.3	7.8	587.4	5	13
B10		.239	.6194	.3732	.0074	35	7.1	8.5	588.1	3	14
B11		.323	.6117	.3806	.0077	35	7.3	7.8	587.3	3	13
B12		.341	.6029	.3867	.0105	35	6.8	7.1	586.4	1	13
D1	Cottonseed oils	.009	.8388	.1612	.0000					1	16
D2		.151	.6063	.3854	.0084	55	5.5	7.3	586.7	3	13
D3		.386	.5884	.3957	.0159	35	5.5	6.1	585.2	1	12
D4		.422	.5822	.4072	.0106	35	4.8	5.3	584.2	4	11
D5		.365	.6115	.3810	.0075	35	7.1	7.7	587.2	3	13
D6		.314	.5967	.3948	.0085	35	6.0	6.5	585.7	4	12
D7		.288	.6176	.3753	.0071			8.3	587.9	3	14
D8		.220	.6135	.3783	.0082	35	6.2	8.0	587.5	2	13, 14
E1	Ga	.493	.5834	.4065	.0101	35	5.4	5.4	584.3	3	11
E2	Tenn	.050	.7146	.2826	.0028	35	23.0	20.5	599.6	3	16
E3	Ala	.224	.6554	.3407	.0039	35	12.7	12.0	592.1	4	15
E4	Ala	.410	.6283	.3661	.0057	35	9.3	9.2	589.0	4	14
E5	Ala	.214	.6675	.3287	.0038	35	14.1	13.5	593.6	3	16
E6	N. C	.426	.5945	.3971	.0085	35	6.2	6.3	585.4	4	12
E7	Ala	.299	.6290	.3647	.0063	35		9.4	589.1	3	14
E8	Ala	.308	.6269	.3667	.0064	35		9.2	588.9	3	14
E9	S. C	.439	.5963	.3949	.0088	35	6.1	6.4	585.6	3	12
E10	Ga	.421	.5954	.3958	.0088	35		6.4	585.5	3	12
E11	Ga	.368	.6030	.3894	.0076	35	7.5	7.0	586.3	4	12, 13
E12	S. C	.411	.6128	.3806	.0066	35	7.5	7.8	587.3	3	13
E13	S. C	.238	.6316	.3617	.0067	35	8.0	9.6	589.4	2	14
E14	N. C	.297	.6207	.3725	.0068	35	8.1	8.6	588.2	3	14
E15	Tex	.392	.6003	.3914	.0084	35	7.6	6.8	586.1	3	12
E16	Ala	.336	.6072	.3847	.0081	35		7.4	586.8	3	13
E17	N. C	.416	.5916	.3994	.0091	35	5.7	6.0	585.2	3	12
E18	N. C	.396	.6002	.3915	.0083	35	7.5	6.8	586.0	3	12
E19	Ga	.406	.6018	.3903	.0080	35	7.0	6.9	586.2	4	12
E20	S. C	.396	.5944	.3969	.0088	35	6.0	6.3	585.4	3	12
E21	N. C	.429	.5965	.3952	.0083	35	7.0	6.4	585.6	4	12
E22	Ga	.374	.5946	.3970	.0085	35	6.0	6.3	585.4	4	12
E23	S. C	.408	.5917	.3995	.0089	35	5.6	6.0	585.1	4	12
E24	Ala	.336	.6073	.3844	.0083	35	6.4	7.4	586.8	2	13
E25	Ala	.295	.6163	.3764	.0074	35	7.4	8.2	587.7	2	14
E26	Ga	.390	.5903	.4014	.0083	35	6.2	5.9	585.0	4	11
E27	Ga	.337	.6038	.3879	.0083	35		7.1	586.4	3	13
E28	Ga	.339	.6113	.3814	.0073	35	7.2	7.7	587.2	3	13
E29	S. C	.240	.6295	.3637	.0068	35	8.0	9.4	589.2	2	14
E30	N. C	.496	.5818	.4080	.0102	35	5.5	5.2	584.1	4	11
E31	Ga	.486	.5852	.4050	.0098	35	5.2	5.5	584.5	4	11
E32	S. C	.502	.5856	.4043	.0102	35	5.5	5.6	584.5	2	11
E33	N. C	.460	.5882	.4025	.0093	35	5.5	5.8	584.8	4	11
E34	Tex	.380	.5957	.3960	.0083	35	6.8	6.4	585.5	4	12
E35	N. C	.369	.6028	.3898	.0075	35	7.2	6.9	586.3	4	12

TABLE 1.—*Colorimetric properties of vegetable oils for a thickness of 5¼ inches*—Continued

NBS lab. no.	Kind of oil or sourse	Sunlight transmittance	Trilinear coordinates			Lovibond grade			Wave length	Spectral transmittance shown in	
						By donor		By NBS on 35Y basis			
		T_s	r	g	b	Y	R	R	λ	Figure	Figure
1	2	3	4	5	6	7		8	9	10	11
E36	Tex	0.298	0.6096	0.3827	0.0077	35	7.5	7.6	587.0	3	13
E37	Ga	.287	.6135	.3790	.0075	35	7.6	7.9	587.4	2	13
E38	Ala	.454	.5918	.3993	.0090	35	6.0	6.1	585.2	3	12
R1	Cottonseed oils	.232	.6473	.3468	.0059	----	------	11.3	591.2	2	15
R2		.405	.6032	.3880	.0088	----	------	7.0	586.4	1	13
R3		.398	.5896	.4022	.0082	----	------	5.8	584.9	4	11
R4		.289	.6124	.3794	.0082	----	------	7.9	587.4	1	13
R5		.261	.6008	.3887	.0106	----	------	6.9	586.2	1	12
R6		.484	.6009	.3902	.0089	----	------	6.8	586.1	1	12
R7		.376	.5970	.3938	.0092	----	------	6.5	585.7	2	12
R8		.340	.6025	.3887	.0088	----	------	7.0	586.3	2	12, 13
F1	Sesame	.103	.6463	.3486	.0051	60	10.7	11.1	591.0	4	15
F2	do	.157	.6102	.3828	.0070	52	7.0	7.6	587.0	4	13
F3	Peanut	.544	.5347	.4485	.0168	25	1.5	1.6	578.8	5	10
F4	do	.638	.5015	.4396	.0589	17	1.0	0.7	577.0	1	10
F5	Soybean	.230	.6083	.3854	.0063	35	7.0	7.4	586.8	4	13
F6	do	.128	.6308	.3643	.0049	65	9.0	9.5	589.2	4	14
F7	do	.082	.6189	.3763	.0048	90	8.0	8.3	587.9	4	14
F8	do	.024	.6344	.3613	.0042	----	------	9.8	589.6	4	14
F9	Corn	.439	.5899	.3968	.0133	----	------	6.1	585.2	1	12
F10	Peanut	.584	.5525	.4245	.0230	----	------	3.4	581.5	2	10
F11	Rape	.423	.5514	.4364	.0122	----	------	2.8	580.7	5	10
F12	S. olive	.442	.5377	.4455	.0168	----	------	1.9	579.2	5	10
F13	C. olive	.100	.5120	.4729	.0151	----	------	−0.2	575.1	5	10
F14	Soybean	.550	.5687	.4198	.0115	----	------	4.2	582.7	5	10

VI. SOME ABRIDGED COLOR-GRADING METHODS

It may be recalled that the specifications of lightness and chromaticity for the vegetable oils, as recorded in table 1 and in figure 8, are all referred to a standard illuminant and colorimetric method, and the properties of the observer are rigidly specified. The method is based on a knowledge of the complete spectral-transmissive properties of the sample and requires extensive equipment and laborious computations to arrive at the desired results. It is essentially a method for the standardizing research laboratory and serves here as the fundamental basis for the discussion and design of abridged color-grading methods for routine application in the field. In the design of such methods, it is generally desirable to avoid the use of a large number of material color standards and to eliminate, if possible, or reduce the effect of the individual-observer variation. Whereas the illuminant and colorimetric method may be readily controlled and standardized, in general the observer must necessarily vary, and his individual color-vision characteristics may introduce serious complications in the colorimetric procedure, depending on the degree of difference existing between the spectral-transmissive properties of the samples to be graded and the color standards defining the chromaticity scale. This difference may exist regardless of the degree of agree-

ment in lightness or chromaticity obtainable between the samples and the standards of color.

It is beyond the scope of the present paper to give a detailed discussion of the application of the Lovibond method—or other abridged colorimetric methods—in the color grading of vegetable oils. The following remarks are included, however, on methods that have been investigated to some extent in connection with the present work, or that are obviously suggested by a consideration of the fundamental data herein presented. The former methods are one-dimensional by design. The latter methods are essentially two-dimensional, but may be reduced to one dimension as previously described, if the simplification is in conformity with practical requirements.

In an attempt to avoid all material color standards and effectively eliminate the properties of the observer, efforts were made during the early part of this work to discover a suitable one-number index to the chromaticity of the oils which could be expressed as a simple functional relationship between transmittances at selected wave lengths in the visible spectrum. An important condition imposed on the problem was the possibility of embodying the method in a practical oil-grading instrument measuring only transmittances at the selected wave lengths. In general, it was found that such abridged spectrophotometric methods were not wholly satisfactory, chiefly because they did not deal adequately with the independent variation of the concentrations of more than one important pigment in the oils. Unavoidable complexities in the experimental and computational aspects of the method made it doubtful if sufficient practical advantage was gained to warrant its routine application in the field.

An attempt was made by Priest [20] and the author to use a small number of selected samples of cottonseed oils as material color standards against which given cottonseed oils might be matched in chromaticity by the proper choice of their thickness alone. The thickness of the oil, or some suitable function thereof, could be used then as a one-number index to chromaticity. A color comparator was constructed in which the sample field was illuminated by a standard illuminant through a controlled variable thickness of the given sample of oil. The comparison field was illuminated by the same source through a fixed thickness of one of the oil standards. Several standards of different spectral type or thickness could be employed if desired. It was found that vacuum-sealed oils devoid of the green pigments were more stable in color than others, but none of the oils investigated proved sufficiently stable over a period of several months to serve as satisfactory color standards. The use of various yellow solutions instead of the oils, as color standards in this method, is suggested by the work of Arny, Kish, and Newmark,[21] but no conclusive investigation has yet been made of the possibilities of such solutions in connection with this variation-in-thickness method.

The classification of the oils into two principal spectral types suggests a color-grading method based on the use of two standard solutions of fixed concentration and of proper spectral type to represent, respectively, the brown and green groups of pigment components in the oils. Light transmitted by variable thicknesses of the solutions

[20] Report of Proceedings of the Sixth Annual Convention of the Society of Cotton Products Analysts, Birmingham, p. 67 (May 1915); Cotton Oil Press p. 87 (July 1919).
[21] J. Ind. Eng. Chem. **11**, 950 (1919).

(in series) would be compared with light transmitted by a fixed thickness of the oil. Then, by suitable choice of a fixed thickness of one solution with a variable thickness of the other, or by varying the relative and absolute thicknesses of both, either one- or two-dimensional chromaticity scales could be established, as desired. The latter variation corresponds precisely to the concentration variation in the vegetable oils. In view of the fact that all vegetable oils may be matched in chromaticity by suitable choice of yellow and red Lovibond glasses, it is certain that the double series of glass standards could be replaced by the two solution standards, which, because of a closer relation to the oil pigments in spectral-transmissive properties, would not only provide the same chromaticity matches but would also reduce the disturbing effect of the color-vision characteristics of the observer. Further investigation is required to discover suitable solutions for these standards which would be satisfactory with respect to stability, reproducibility, and spectral transmittance.

An inspection of the (r,g) diagram in figure 8 shows that a convenient and reproducible one-dimensional chromaticity scale is provided by the regular sequence of spectrum colors. From the reddest vegetable oils through the range of prime cottonseed oils the spectrum colors and the oil colors are nearly equal in chromaticity. This close agreement holds also for some very light oils of the F group. The evaluation of the oil colors on this wave-length scale has been described in section IV, and the λ values recorded in column 9 of table 1, for the standard observer on the OSA colorimetric system. Unfortunately, any attempt to incorporate this simple chromaticity scale into a practical color-grading method must seriously involve the color-vision characteristics of each different observer assigned to the color measurements. This condition follows from the wide difference in spectral-energy distribution existing between the light transmitted by the oils and that of a narrow wave-length band centered at the λ value required to obtain the nearest chromaticity match with the oils. It is known that under such conditions normal observers would vary in their individual λ values by amounts equivalent to 2 or 3 red units on the scale of $35Y+N''R$. Hence, the use of this method would require a separate calibration of each observer making the color measurements. This would call for perhaps several glass or liquid filters standardized for the purpose and having spectral-transmissive properties approximating closely those of the oils. The added complication in the colorimetric procedure nullifies the apparent advantages of this simple basis for color grading.

It is also shown in figure 8 that a system of standard colors slightly less saturated than the pure spectrum colors is required to obtain exact chromaticity matches with all the oils. This condition could be realized by an extension of the method just described in which the pure spectrum colors would be diluted slightly by admixture with a variable amount of "white" light from the standard illuminant. A two-dimensional chromaticity scale is thus established by the independent variation of both wave length and purity, but the method is subject to the same pratical objections as the simpler method just described.

Another extension of the simple spectrum method is possible which would largely eliminate the variation in scale settings obtained by different observers. Instead of using a narrow band of wave lengths, alone or admixed with white, the chromaticity of an oil could

be accurately matched by use of a single wide band of wave lengths, covering roughly the same wave-length range as is transmitted by the oil itself.

In a colorimeter based on this principle, the comparison field would be illuminated by light from the standard illuminant after transmission through a selective light filter consisting essentially of the slit-lens-prism arrangement of an ordinary monochromator used with exceptionally wide slits. A control of the widths, position, and form of the slits would provide a wide variation in form of the curve of spectral transmission for this filter. In particular, all wave lengths in the red could be transmitted, as is done by the oils, and all wave lengths shorter than a certain value cut off completely. The cut-off could be made abrupt or gradual, as desired, to simulate most closely the spectral-transmissive properties of the oils. It may be recalled that this is the condition required to reduce or eliminate from the method the variable color-vision characteristics of the observer, and may be satisfied in this method perhaps even better than is done by the use of Lovibond-glass combinations. The sample field of the colorimeter would be illuminated by the standard illuminant through a fixed thickness of oil, and independent means provided for equalizing the brightnesses of the sample and comparison fields.

The chief advantage of this method lies in the avoidance of all reference to material color standards. Again, as in other color-grading methods herein considered, one- or two-dimensional chromaticity scales could be established, as desired, the scale variables being related to instrumental parameters involving the position, width, or form of the slits. Considerable research and development work would be necessary to determine the best procedure in the practical application of the method.

In regard to all color-grading methods, it may be noted that scale variables in one method are always convertible into corresponding scale variables in another method. Such conversions are illustrated in the present paper by the transformation of scale values in the OSA system to values on the special N'' scale and the λ scale. In accordance with the single or double dimensionality of the scales, we deal respectively with nearest or exact chromaticity matches. Hence, it is always possible, upon the adoption of any improved method for the color grading of vegetable oils, to supply conversion tables along with the method, or perhaps to calibrate the scale of the colorimeter itself, so that results could be given in Lovibond terms until it is deemed desirable to use only the terms suited to the revised grading system itself.

VII. SUMMARY AND CONCLUSIONS

1. The spectral-transmittance and colorimetric properties of 125 vegetable oils are presented in tabular and graphical form. The investigation includes 111 cottonseed, 3 peanut, 5 soybean, 2 sesame, 1 rape, 1 corn, and 2 olive oils.

2. The oils in a 5¼ inch thickness, may be classified roughly into two general spectral types, determined, respectively, by the varying concentrations of two principal groups of pigment components. One group includes the green materials derived from chlorophyll; the other group includes perhaps several yellow or amber-colored materials of unknown identity.

3. With respect to spectral-transmissive and colorimetric properties, there is no essential difference between the cottonseed and the other vegetable oils included in this investigation. Hence the problem of color grading over the range of cottonseed oils apparently encompasses that for all vegetable oils.

4. The spread in lightness over the group of vegetable oils is greater than can be conveniently matched in the present method of color grading, in which the number of clear and colored glasses used with the Lovibond tintometer is varied while maintaining the best chromaticity match in the fields of the instrument. An improved color comparator is desirable, providing a more suitable arrangement for equalizing brightnesses of the sample and comparison fields.

5. The independent variation in relative and absolute concentrations of the several pigments present in the oils, makes it impossible to represent all oils accurately on any one-dimensional chromaticity scale. For accurate color grading in the Lovibond system, this situation demands the introduction into trade practice of a two-dimensional Lovibond scale established by the independent variation of both yellow and red. It is shown that the best yellow numeral varies approximately from 20 for very light cottonseed oils to 80 or above for the prime yellow oils. An improved one-dimensional Lovibond scale would be provided by the fixation of yellow in some definite relation to red.

6. A brief discussion is given of some color-grading methods based on the following principles:

(1) The measurement of transmittances at a few selected wave lengths and the combination of these quantities in suitable relation to one another to yield a satisfactory one-number index to chromaticity.

(2) The grading in terms of a variable thickness of a sample oil required to obtain a nearest chromaticity match with a fixed thickness of a standard oil or standard solution.

(3) The grading of a fixed thickness of the sample oil in terms of the variable thicknesses of two standard solutions of fixed concentration (in series), representing, respectively, the brown- and green-pigment groups in the oils.

(4) The use of a variable light filter constructed on the principle of the well-known monochromator, but provided with special control of the position, width, and form of the slits, so that the spectral transmission of the filter could be controlled and made to conform as closely as possible to the spectral transmission of the oils to be graded.

7. Some experimental work is described on the application of methods (1) and (2) to cottonseed oils. It was found, however, that the oils themselves were not sufficiently stable in color to serve as satisfactory color standards. Other possible standards were not investigated. Both methods were deemed unsuitable for routine commercial application, however, chiefly because of complications involving the independent variation in concentration of more than one important pigment in the oils. Each of these methods was designed to establish a practical one-dimensional chromaticity scale. Methods (3) and (4) provide the possibility of either one or two-dimensional scales for all oils, but no experimental work has been done on the methods. They are suggested by the fundamental data presented in the paper.

WASHINGTON, May 10, 1935.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP816

Part of Journal of Research of the National Bureau of Standards, Volume 15, August 1935

FACTORS AFFECTING ULTRAVIOLET SOLAR-RADIATION INTENSITIES

By W. W. Coblentz and R. Stair

ABSTRACT

Ultraviolet-filter transmission measurements are made, using a newly devised portable precision ultraviolet meter (Research Paper RP647) and 4 glass filters, giving the special quality and total intensity in the band of ultraviolet solar radiation extending from about 2900 to 3500 A. At the high-altitude station (Flagstaff, Ariz.) data were obtained on solar ultraviolet intensities under various conditions; high and low humidity, large and small air masses, clear and smoky skies. The data obtained at sea-level stations (Washington, D. C., and San Juan, P. R.) are of interest in connection with the question of ultraviolet intensities in the tropics as compared with similar stations at higher latitudes.

Data are given on the amount of ultraviolet transmitted through light fog, and on the amount reflected by the sky and by snow; also the effect of altitude and latitude on the solar ultraviolet intensity at the earth's surface.

The observations show that, while a light fog greatly reduces the intensity (when the sun appeared as a distinctly outlined white disk, the intensity was reduced to one-tenth or less) the spectral quality was practically unchanged, owing to the relatively nonselective character of the transmission through water vapor. Similarly, the ultraviolet reflected from snow is extraordinarily high, owing to the fact that the ice crystals, within which the reflection occurs, are highly transparent to ultraviolet radiation.

The absorption of ultraviolet is caused by atmospheric polution near the earth's surface, and by ozone in the stratosphere. An increase of 40 to 50 percent in intensity in the band of wave length between 2900 and 3130 A, is observed in rising 2 km (7,000 ft) above sea level. A much greater increase in intensity may be expected at elevations of 15 to 25 km (10 to 15 miles). However, such heights are not practicable for large-scale biological tests.

The measurements at the Flagstaff station show a greater atmospheric transparency (less ozone) in the afternoon than in the forenoon; and a greater transparency in the autumn than in the spring. This is in agreement with the work of Dobson and others, using other methods of observation.

For the same solar altitude (air mass traversed by the rays) the ultraviolet solar intensities in the tropics (at San Juan) were somewhat higher than at a midlatitude, sea-level station (Washington) that is free from local air pollution. This is in agreement with other observations showing that, in the tropics, for the same solar altitude, the amount of atmospheric ozone is less, and consequently the ultraviolet intensities should be somewhat higher than in higher latitudes.

However, this small difference in intensity, for the same solar altitude, does not appear to be sufficient to produce marked differences in biological effects. If differences in biological effects ascribable exclusively to a difference in ultraviolet intensities are observable, they may be owing to the fact that for about 4 months (April 20 to August 20) at the noon hour, in the tropics, the sun shines through an air mass of $m=1.00$ to 1.01, as compared with an air mass of $m=1.04$ to 1.05 in midlatitude (Washington). Consequently, during this period, the shortest—biologically most effective—wave lengths (at 2900 to 3000 A) are very greatly increased in intensity. The average intensity of the whole spectral band (at 2900 to 3130 A), recognized as having a specific biologic action, at least in curing rickets) during the time when the sun shines through an air mass of $m=1.00$ to 1.01, is about 20 percent higher in the tropics than is ever attained in midlatitude.

Similarly, during the 5 winter months, at midlatitude stations, the shortest—biologically most effective—ultraviolet wave lengths are almost completely absorbed, and the intensity of the less effective wave lengths is less than one-sixth the value that obtains in the tropics.

In addition to the greater intensity of the ultraviolet, there, usually is also a greater number of hours of sunshine in the tropics during the winter months. Other factors to be considered are differences in air movement, temperature, humidity, and the amount of clothing worn, all of which factors have an effect upon the incidence of rickets, which is practically unknown in the tropics.

CONTENTS

		Page
I.	Purpose and simplified method of ultraviolet solar radiometry	124
II.	Climatic conditions at the observing stations	139
III.	Minor observations	140
	1. Fog	141
	2. Snow	141
	3. Sky	142
	4. Erythema tests	142
IV.	Effect of altitude on ultraviolet solar radiation	143
V.	Effect of geographic latitude on ultraviolet solar radiation	147
VI.	References	150

I. PURPOSE AND SIMPLIFIED METHOD OF ULTRAVIOLET SOLAR RADIOMETRY

A knowledge of the intensity and spectral quality of short wave length ultraviolet solar radiation is of great importance in climatology, physiology, and biology.

The interest of the National Bureau of Standards in this subject is in methods of exact evaluation of the spectral band of ultraviolet solar radiation, of wave lengths extending from about 3200 A to the limit of transparency of the earth's atmosphere at about 2900 A, which is recognized as having a specific effect in preventing and healing rickets, and on this basis is being used as an adjunct in medicine.

The object of the present communication is to describe measurements of the spectral quality of short wave length ultraviolet solar radiation, at different stations, as affected by the altitude of the sun, by the geographic latitude and the altitude of the observing station, and by different atmospheric conditions. In a future communication a description will be given of recent developments in the exact evaluation of ultraviolet radiation in absolute units.

The ultraviolet intensities are measured by means of a newly developed radiometer (1) [1] consisting of a titanium photoelectric cell, which responds only to the spectral band under consideration, and a balanced amplifier (fig. 1) for measuring the weak photoelectric currents induced in the photoelectric cell by ultraviolet radiation. By means of a group of four glass filters this spectral band of ultraviolet (extending from about 2900 A to 3500 A) is separated into 5 parts. In this manner it is possible to determine, in a few minutes, the shape of this part of the solar spectral-energy curve, apparently as accurately as has thus far been possible with a spectroradiometer. The latter method consumes a much longer time to make the observations, which, in addition, require numerous corrections, including adjustments for changes in atmospheric transmission during the measurements.

[1] The figures in parentheses here and elsewhere in the text refer to the literature references at the end of this paper.

Research Paper 916
Journal of Research of the National Bureau of Standards

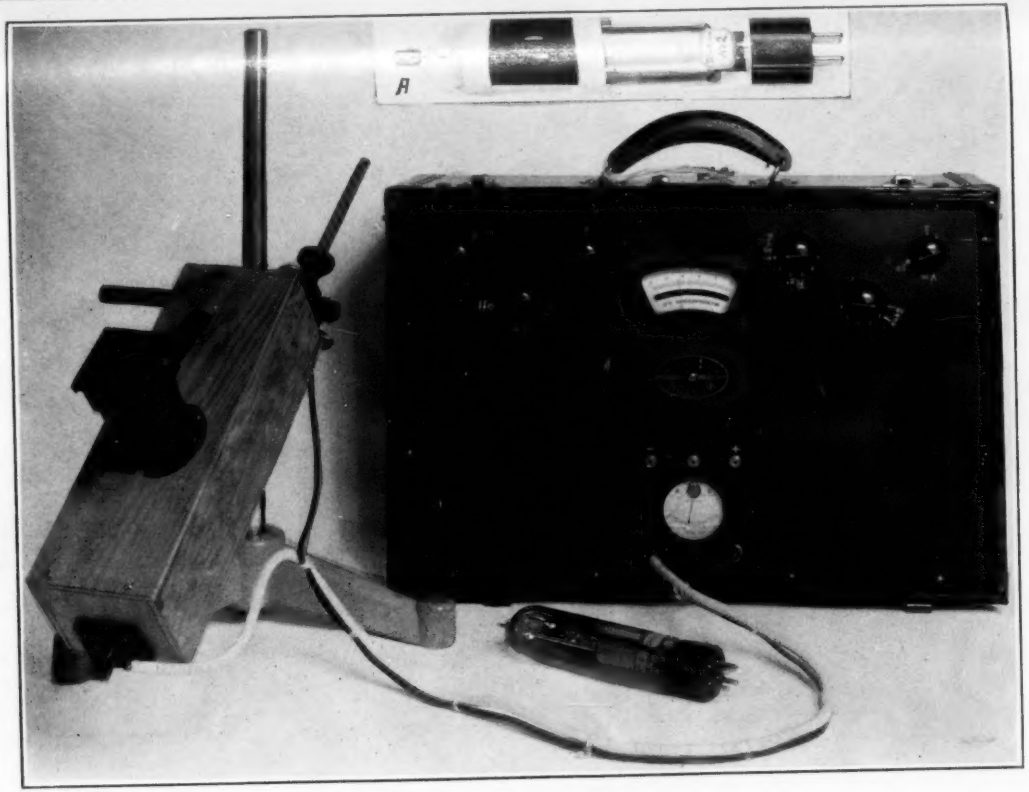

FIGURE 1.—*Ultraviolet meter.*

This consists of a titanium photoelectric cell (left, mounted on polar axis; unmounted cell in center foreground and in inset *A*) and balanced amplifier.

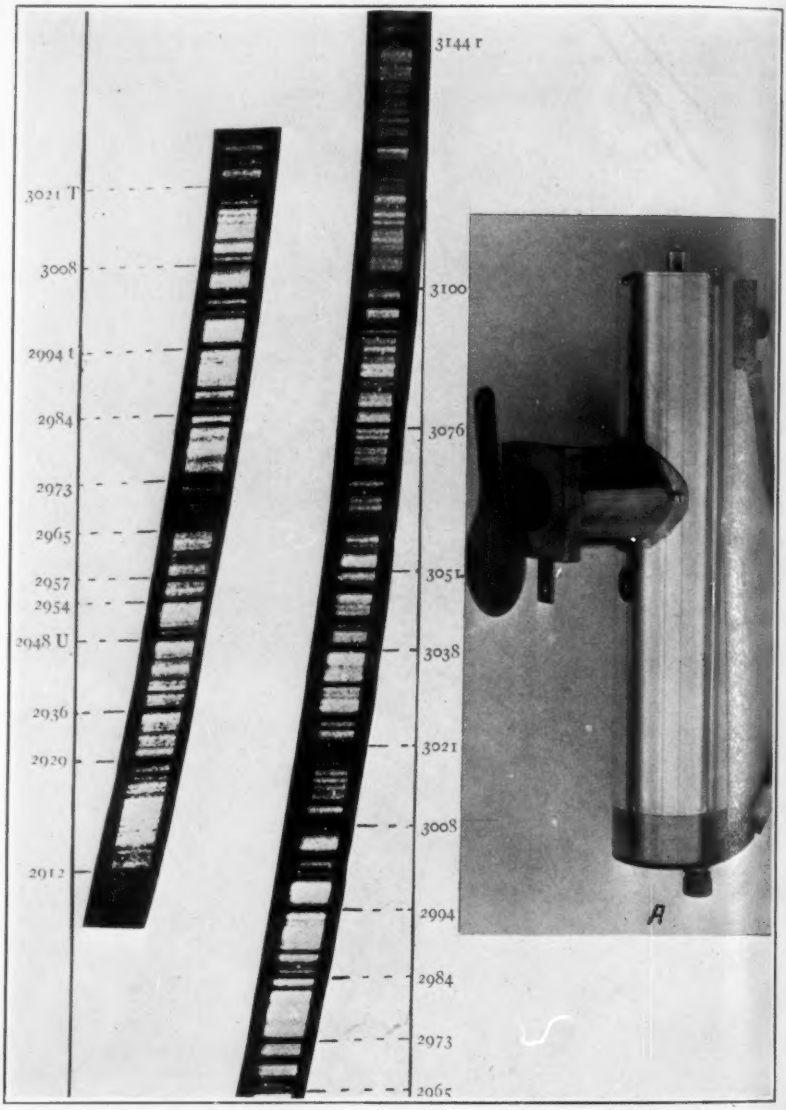

FIGURE 2.—*Ultraviolet end of the solar spectrum, obtained by Fabry and Buisson, at Marseille in June 1920.*

By means of a focal-plane shutter, which occulted different parts of the spectrum, in going from 3020 to 2930 A the time of the exposure was increased in the ratio of from 1 to 1,000.
A is a metal container for the photoelectric cell (see fig. 1).

In both methods, wide bands of the spectrum are measured. Hence, owing to the small dispersion that can be used, the observed spectral-energy curve, in the region of 2900 to 3500 A appears to be relatively smooth and free from indentations (2); whereas, using a high dispersion and a narrow slit, photographs (3) show the spectrum deeply indented with absorption lines, caused by vapors of various elements in the solar atmosphere and by varying degrees of concentration of ozone in the terrestrial atmosphere (fig. 2). Recalling (3) the fact that the intensity of solar radiation at 3143 A is about 1 million times that at 2898 A, and that the intensity throughout this whole spectral region is extremely low, it will be evident to the reader that it is practically impossible to obtain, radiometrically, a solar spectral-energy curve, accurately showing the indentations by the absorption lines indicated in the spectrum photographs.

Hence, for the purpose of the present work, the evaluation of the spectral-energy curve that gives calculated filter transmissions which are in agreement with the observed values is probably as accurate as the spectral-energy curve determined directly with a spectroradiometer. In fact, from the highly selective response of the photoelectric cell in the region of 2900 to 3000 A, slight variations in ultraviolet intensity in this spectral region (in which we are especially interested) are more easily and more accurately determined by the integrated measurements with the filters than with a spectroradiometer, because of the accompanying losses in intensity by absorption in the optical system and in the auxiliary reflecting apparatus.

The experimental procedure of the investigation now in progress consists in observing the variation in the total intensity of the ultraviolet radiation in the band of wave lengths extending from about 2900 to about 3500 A in sunlight, throughout the day and throughout the year, by means of titanium photoelectric cells having the spectral response curves illustrated in figure 3. At the same time, the percentage transmission of this band of radiation through a set of four glass filters (designated Corex D, Nillite, Ba-flint-1, and Ba-flint-3, having the spectral-transmission curves illustrated in fig. 3) is determined. The variation in transmission of this band of ultraviolet radiation, through any one filter, with variation in solar altitude, air pollution, geographic latitude, etc., indicates a variation in spectral quality—the higher the transmission, the lower the intensity of the radiation of the shortest wave lengths.

Data of this type are illustrated in figures 4 and 5, which depict the observations made at the Lowell Observatory, Flagstaff, Ariz. (elevation 7,300 ft.) during the summer of 1934.

The next step is to determine, by calculation, the shape of the spectral-energy curve required to give the observed transmissions of ultraviolet through the 4 filters. For this purpose, in the first trial calculation, use was made of the average ultraviolet solar spectral energy curve observed by Pettit (2) at Tucson, Ariz. (elevation about 2,500 ft), in May 1931. The product of this spectral-energy curve and the spectral response curve of the photoelectric cell (fig. 3) gives the solar spectral-energy curve as it affects the particular photoelectric cell employed in making the measurements (fig. 6).

For example, curve "Ti No. 1" in figure 6 is the shape of the solar spectral-energy curve as it would be observed by the uncovered titanium photoelectric cell no. 1. The product, at each wave length,

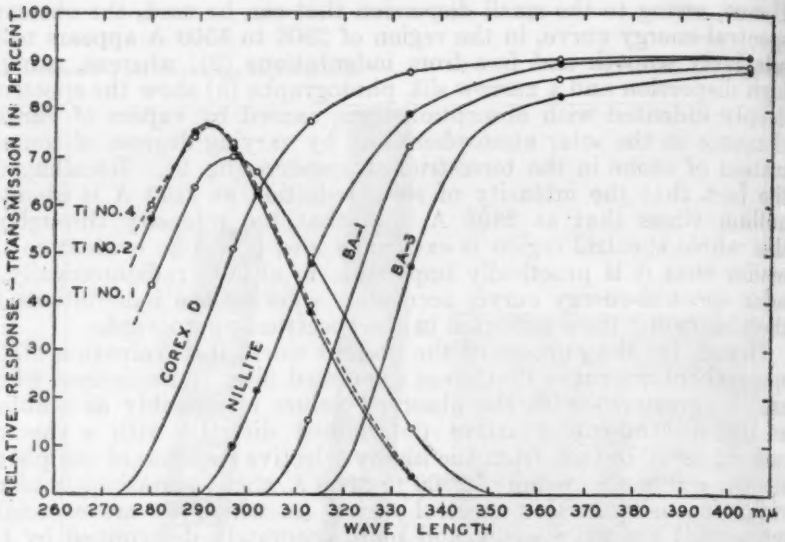

FIG. 3.—*Relative response curves of titanium photoelectric cells nos. 1, 2, and 4, to an equal-energy spectrum; also spectral transmission of the glass filters used—Corex* D, *Nillite (both trade names), and barium-flint glass* (Ba–1 *and* Ba–3, *thickness 1* mm *and 3* mm, *respectively*).

Wave lengths 400 mμ= 4000 A

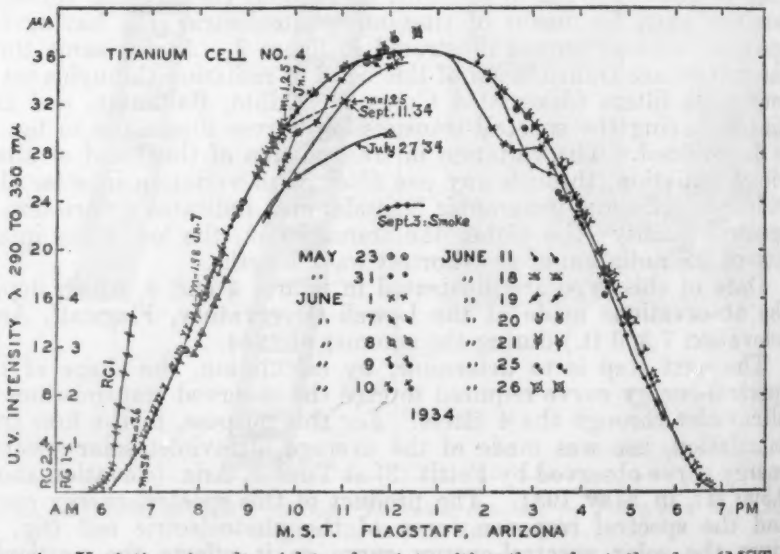

FIG. 4.—*Variation in ultraviolet solar intensities throughout the day* (MST= *mountain standard time) and as affected by smoke.*

The ordinates are readings on the micrometer; amplifier sensitivity, Rg. 1=1.57 Rg. 2. Observations made at Flagstaff, Ariz., elevation 7,300 ft.

of this spectral energy by the corresponding percentage transmission of the filter (fig. 3) gives the spectral-energy curves marked Cx., Ni., Ba–1, and Ba–3, in figure 6. The ratios of the areas under these curves to the area under the curve, Ti No. 1, gives the calculated

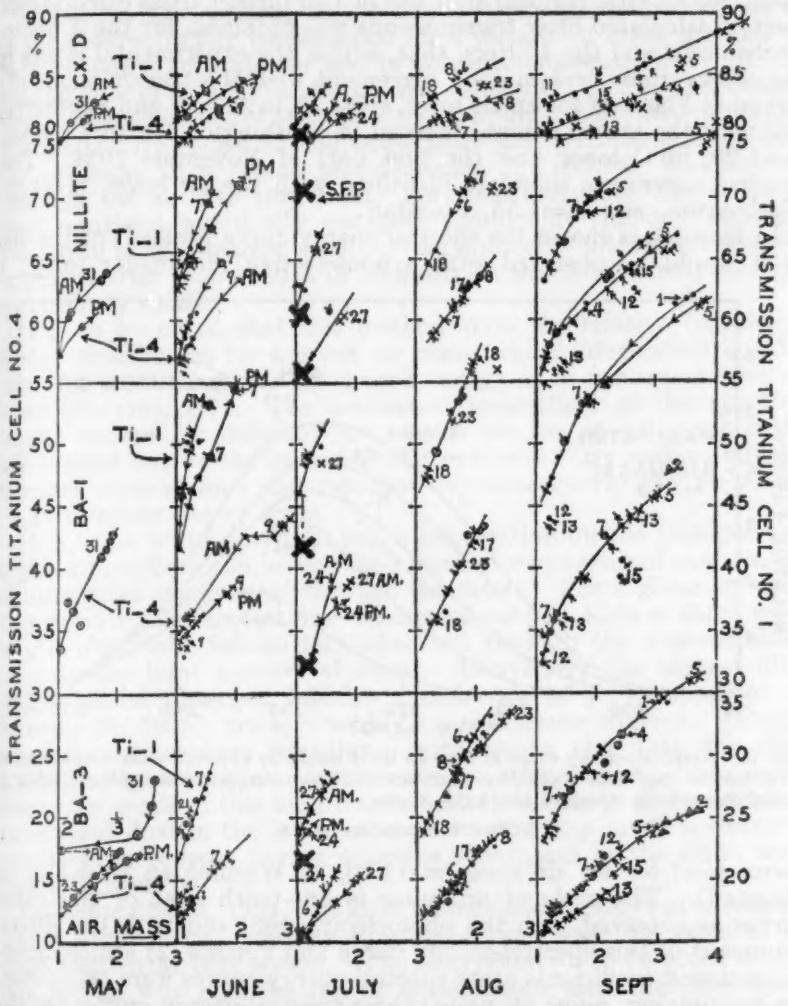

FIG. 5.—*Variation in transmission of ultraviolet solar radiation through the various filters* (Ba–3, *etc.*) *with solar altitude* (*air mass, m=1, 2, 3*), *time of the day* (*a.m.; p.m.*) *and the season, as observed with 2 photoelectric cells* (Ti–1 *upper sets of curves;* Ti–4, *lower sets of curves* (*see fig. 3 for spectral response*)).

The numbers (1, 7, 24, etc.) are the dates of observation. The heavy crosses (× × ×, S.F.P.) indicate observations on the San Francisco peaks (Fremont Saddle, elevation 10,500 ft).

percentage of ultraviolet transmitted through the filters. Similar curves were obtained for the titanium photoelectric cell no. 4.

From the deviations of the calculated from the observed filter transmissions, which were in agreement for both photoelectric cells, it was apparent that the spectral intensities indicated in Pettit's

energy curve, in the region of 2950 to 3050 A, were slightly too high, and the intensities at 3250 A to 3550 A were appreciably too low, to fit the observations of 1934 at the higher elevation (7,300 ft.) at Flagstaff, Ariz. By making slight changes in the energy curve in these two spectral regions, after one or two further trials calculations, a set of calculated filter transmissions was obtained, for the 2 photoelectric cells and the 4 filters, that, within the experimental errors in the observations, was in good agreement with the transmissions observed at Flagstaff for an air mass, $m=1.35$, in August and September and with the transmissions observed in Washington for an air mass, $m=1.20$, in October and the first part of November 1934. This spectral curve was therefore identified with the air mass, $m=1.20$, Washington, and $m=1.35$, Flagstaff.

In figure 6, is shown the spectral energy curve (dotted) of the sun as it would be observed with a nonselective radiometer (e. g., a

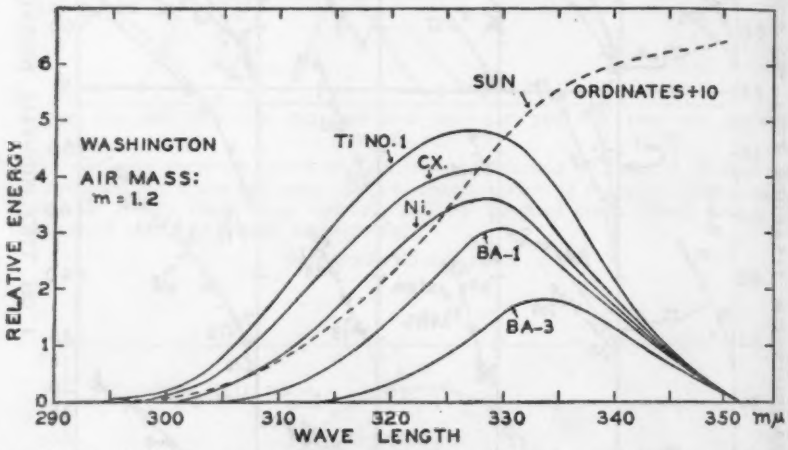

FIG. 6.—*Spectral-energy curve of the sun as it would be observed with a nonselective radiometer and with a selective photoelectric radiometer, without a filter,* Ti *No. 1, and through the standard filters* Ba–3, *etc.*

Wave lengths 350 mμ=3500 A

thermopile) for an air mass, $m=1.20$, at Washington ($m=1.35$ at Flagstaff). The scale of ordinates is one-tenth that of the other curves as observed with the photoelectric cell, and with the filters. By means of this spectral-energy curve and Pettit's (2) atmospheric-transmission coefficients other spectral-energy curves were calculated. On multiplying, point by point, these spectral-energy curves by the spectral-response curves of the 2 photoelectric cells and by the spectral transmissions of the respective filters, as indicated above (see fig. 3) calculated transmissions were obtained for the 4 filters, using 2 photoelectric cells, which (after one or two trial adjustments of the assumed spectral-energy curve) were in close agreement with the observed filter transmissions for air masses $m=1.05$, 1.10, 1.25, 2.20, and 3.05 at Flagstaff, and with the observed transmissions for correspondingly smaller air masses in Washington.

In view of the fact that the atmospheric transparency, for a given air mass, may vary from morning to afternoon, with the season, and with the ultraviolet emission of the sun (as affected by sun spots), no attempt is made to identify the calculated with the observed filter

transmissions closer than air mass $\Delta m=0.05$. If great refinements are attempted, the spectral-energy curve corresponding with the filter transmissions, observed at the time of the physiological tests, should be used instead of a standard curve corresponding with the solar altitude at the time of the test.

The ultraviolet spectral-energy curve, calculated in this manner to fit the observed filter transmission for a certain air mass, appears to be sufficiently accurate for use in the evaluations desired. If the method should be adopted for general use, only 1 or 2 filters, having integral transmissions of 30 to 60 percent, would be necessary; although it is instructive to use an additional filter that transmits 80 percent. For example, in a recent test (January 2, 1935) in Washington, although the air was very clear,[2] the transmission of the Corex-D filter remained practically constant throughout the day, showing that, even in the clearest weather, the amount of ultraviolet of wave lengths shorter than 3020 A in midlatitude, sea-level, winter sunlight is extremely small.

It is to be noted that this method gives the relative (intensity) energy distribution for a given air mass, which information is sufficient for evaluating the integrated energy in a particular spectral band (6), (16), (17). The ordinates (intensities) of the spectral-energy curves for different air masses are on an arbitrary scale, which need not be the same for all the curves. By making supplementary observations and calculations, these curves can be placed on an absolute energy basis.

It is to be noted also that much information on the transparency of the atmosphere can be obtained from a comparison of the amount of ultraviolet transmitted through the filters. For a given air mass (say $m=1.1$) the lowest filter transmissions (the highest short wave length ultraviolet intensities), observed through the clearest skies, indicate the least amount of ozone. Conversely the highest filter transmissions, observed through a clear sky (e. g., as observed on January 24, 1935), are ascribable to a high ozone content. Usually when the atmosphere is polluted with smoke and dust, the filter transmissions are high. In this case, no attempt is made to determine how much of this high transmission is owing to the presence of smoke and dust in the lower atmosphere and how much is owing to ozone—both sources having selective absorption in the short wave length ultraviolet.

On September 3, 1934, the filter transmissions observed through a smoky atmosphere, contrary to expectations, were the same as for clear weather at that season. The interpretation to be given is that this smoke was nonselective in transmission and that the ozone content was low (the ultraviolet intensity in the shortest wave lengths was high) in accordance with the season.

At the higher altitude (Flagstaff) local, almost imperceptible, changes in atmospheric transparency are easily recorded by ultraviolet radiometry. For example, on September 13, 1934, which was one of the clearest days of the season, the ultraviolet filter transmissions were very low, corresponding with a low ozone content (a high

[2] One criterion for judging clearness is a low-hanging, dark haze on the horizon, NNE. of the National Bureau of Standards, visible on the clearest days, and apparently identified with the "city haze" over Baltimore, some 35 miles away.

intensity of short wave length ultraviolet). The sky radiation was low. Nevertheless, owing to an imperceptible temporary, local pollution (or more likely an increase in ozone at the noon hour) the filter transmissions were perceptibly higher at the noon hour than at 10 a.m.

It is to be noted that a slight difference in the spectral response curves of two photoelectric cells has a noticeable effect upon the filter transmissions when the measurements are made under constant atmospheric conditions. For example, as illustrated in figure 3, the photoelectric cells Ti No. 2 and Ti No. 4, differ but little in spectral response—Ti No. 4 apparently being slightly more sensitive in the shortest wave lengths and slightly less sensitive in the longer wave lengths. The filter transmissions observed with photoelectric cell Ti No. 4 should, therefore, be slightly lower than with Ti No. 2. Careful measurements on the filter, Ba-3, through practically the same air mass (September 11, 1934, $m=1.22$) gave a transmission of 12.2 percent using Ti No. 4, and 13.1 percent using Ti No. 2, in agreement with expectations.

It is impracticable to discuss all the observed data, some of which are given in table 1. A study of these data reveals interesting information indicating the constancy of atmospheric conditions as shown by the same percentage transmissions of the filters for the same solar altitudes, on widely different dates; for example (table 1, colums 7 and 8) the measurements on June 22 and July 6, $m=1.27$; also the early morning measurements on June 9 and August 8, 1934, $m=2.04$. Again, at 8 to 9 a.m., the sky was clearer on September 12 than on September 7, giving the same filter transmissions for larger air masses.

At high altitudes slight changes in atmospheric conditions produce marked changes in the filter transmissions, as noted on September 13 (one of the clearest days) as compared with September 12 and 14, 1934. August 27 and September 5 are typical of sudden changes in sky conditions. June 10 was typical of a low humidity (press aq. vap.=1.58 mm) and the attendant difficulty of keeping the filters free from fine dust which was attracted by electric charges on the glass. June 9 was a good day to obtain data from early morning to late afternoon (fig. 4).

TABLE 1.—*Filter transmissions of integrated ultraviolet solar radiation for different air masses, m, using a titanium photoelectric cell, Ti No. 4 (see fig. 3).*

[Filters: Ba-3 = barium flint, thickness 3.12 mm; Ba-1, same, thickness 1.00 mm; Ni. = Nillite (trade name); Cx. = Corex D (trade name) (see fig. 3). Tr = percentage transmission. The intensity is the microammeter-scale reading (μa) for Rg. 2, and amplifier sensitivity = 12.1. Observations made at Flagstaff, Ariz. (latitude 35°12′ N, altitude 7,300 ft), in 1934. The time is mountain standard time; 26 min, 45 sec faster than local time. The dagger, †, and asterisk, *, are used to associate intensity with air mass]

1	2	3	4	5	6	7	8	9	10	11
Date, 1934, and time	Intensity	Ba-3		Ba-1		Ni.		Cx.		Remarks
		m	Tr	*m*	Tr	*m*	Tr	*m*	Tr	
May 23:	μa									
8:10 to 8:55 a.m.	† 20.0 to 25.2	† 1.90 to 1.53	16.5 to 14.5							Sky perfectly clear to horizon all a. m.; slight haze (perhaps smoke) in p. m.
11:15 to 11:45 a.m.	36.0	1.07	12.2	1.07	33.5	1.06	57.1	1.05	79.5	
3:35 p. m.	25.5	1.37	14.2							
May 31:										
6:35 to 6:50 a.m.	† 2.6 to * 7.8	† 3.63 to * 3.37	23.0 to 18.5	3.53 to 3.47	54.0 to 52.0					
7:56 a.m.	15.0	2.04	17.4							
7:58 to 8:40 a.m.	† 15.3 to * 20.5	† 2.00 to *1.60	17.0 to 14.5	1.91 to 1.78	42.7 to 40.8	1.84 to 1.71	63.8 to 63.2	1.68 to 1.66	82.8 to 82.6	Clear after several days of rain; slight haze in valley southeast of Elden Mountain at 7 to 8 a.m. Temperature = 69° F at 4:15 p. m.
9:50 to 10:02 a.m.	† 30.2 to * 31.5	† 1.25	13.7	1.24	36.7	1.23	60.8	* 1.22	81.3	* Light smoke from incoming train, perhaps 15 miles to the west. ♭ No smoke; but more corona. Press. aq. vapor = 3.6 mm.
2:18 to 2:58 p.m.	† 32.6 to * 26.8	† 1.15	12.9	1.17	37.3	1.20	60.5	* 1.21	♭ 82.5	
3:35 to 4:04 p.m.	† 26.0 to * 21.7	† 1.34	12.1	1.39	35.5	1.43	59.5	* 1.48	♭ 81.3	
5:15 to 5:26 p.m.	† 10.3 to * 8.7	† 2.18 to * 2.34	16.5 to 16.8							

TABLE 1.—*Filter transmissions of integrated ultraviolet solar radiation for different air masses, m, using a titanium photoelectric cell,* Ti *No. 4 (see fig. 3)*—Continued

1	2	3	4	5	6	7	8	9	10	11
Date, 1934, and time	Intensity	Ba-3		Ba-1		Ni.		Cx.		Remarks
		m	Tr	*m*	Tr	*m*	Tr	*m*	Tr	
June 1:	μa									
10:29 to 10:46 a.m.	†31.0 to *34.2	†1.15	14.3	1.13	35.5	1.12	58.6	*1.11	▪79.2	▪ Smoke 9:30 to 11 a. m., see figure 4.
11:25 to 11:48 a.m.	†34.8 to *37.0	†1.06 1.04	13.1 12.8	1.05	34.8	1.04	56.8	*1.04	78.9	▸ Smoke, 2 to 3 p. m.
2:04 to 2:34 p.m.	†30.5 to *28.3	†1.11	12.4	1.12	32.7	1.14	57.8	*1.15	▸81.5	◦ No smoke; more haze at 3 to 4 p. m.
3:09 to 3:35 p.m.	†28.0 to *22.5	†1.25 1.29	12.2 12.5	1.33 1.35	35.3 35.7	1.37	60.6	1.41 *1.53	◦81.0 81.5	Press. aq. vap.=4.6 mm at 8:45 a. m., and 2.4 mm at 4:25 p. m.; temperature=73° F.
June 5:										
10:30 to 10:53 a.m.	†31.3 to *32.2	†1.14 *1.10	13.3 13.8	1.13	36.0	1.12	59.1	1.11	82.1	Sky very clear; no corona at noon.
12:04 to 12:20 p.m.	†36.2	†1.04	12.0	1.04	30.6	1.04	56.9	1.04	79.5	Press. aq. vap.=19.5 mm; temperature=66° F at 4 p. m.
2:31 to 2:51 p.m.	29.8 to *23.7	1.16	13.0	1.17	29.7	1.18	57.8	*1.19	80.7	
June 7:										
5:45 to 6:12 a.m.	†0.01 to 0.35	†5.80 4.70								
6:15 to 6:30 a.m.	†0.78 to 2.02	†4.65 4.10								Sky clear blue after snow and hail of June 6.
6:34 to 8:00 a.m.	†2.35 to 14.8	†3.95 1.95								Press. aq. vap.=1.98 mm; temperature=57° F at 11 a.m.
8:05 to 8:32 a.m.	†16.1 to *19.6	†1.88 1.69 *1.64	17.3 16.3 15.7	1.83	43.3	1.78	64.8	1.75 1.72	82.3 81.7	

June 9:										
6:51 to 7 a.m.	†4.5 to *5.8	†3.25 *3.02								
7:06 to 7:17 a.m.	†6.8 to *8.0			†2.88 2.80 2.73 *2.62	44.0 43.2 43.5 42.5					Light westerly breeze. Sky clear blue, no smoke.
7:38 to 7:59 a.m.	†11.7 to *14.6	†2.22	12.5	2.12	42.7	• 2.04	• 63.3	1.98 *1.95	82.5 82.2	• See August 8th.
10:45 to 11:08 a.m.	*34.8	*1.07	11.6	1.08	34.4	1.10	56.5	1.09	79.8	Zenith sky radiation=0.12 μa at 12:05 p.m.; =0.01 μa at 6:45 p.m.
1:55 to 2:23 p.m.	†35.9 to *32.2	†1.08	13.9	1.09 1.10	35.3 34.5	1.11 1.12	55.3 56.0	1.12 *1.13	81.5 81.3	At 6 p. m., sky is clear to horizon, small corona. (See figure 4.) Press. aq. vap.=2.3 mm; temperature=71° F at 12:25 p.m.
3:35 to 4:42 p.m.	†27.0 to *16.5			†1.35 *1.82	35.3 38.0					
6:15 to 6:45 p.m.	†2.7 to *0.5	†3.75 *5.20								
June 10:										
10:20 to 10:47 a.m.	†31.7 to *34.0	†1.14	11.8	1.13	34.9	1.11	56.7	*1.10	79.8	Sky radiation 30° north and 30° east of zenith=0.16 μa at 11:50 a.m. Erythema produced by 9-minutes exposure at 1:15 p. m. Dust collects on filters; static charge on glass. Press. aq. vap.=1.58 mm at 12:45 p.m.; temperature 76° F.
June 19:										
9:30 to 9:52 a.m.	†27.8 to *30.1	†1.29 1.28	13.2 13.3	1.27 1.26	36.6 36.3	1.25	58.7	1.24 *1.22	79.5 79.6	Sky radiation=0.15 μa north and east of sun at 11:55 a.m. Thin smoke at 11:10 a.m. Press. aq. vap.=3.0 mm at 12:45 and 4:45 p.m.; temperature=72° F.
10:44 to 11:10 a.m.	†33.4 to *34.4	†1.09	12.3					*1.07	81.5	
2:50 to 3:20 p.m.	†29.4 to *28.7	†1.20 1.23	12.7 13.5	1.25	33.9	1.28	58.0	1.29 *1.30	81.3 81.1	
June 20:										
9:35 to 10:33 a.m.	†29.3 to *34.5	†1.28 1.27	13.0 13.1	1.20 1.19	36.2 36.3	1.18	59.3	1.15 *1.12	• 81.7 80.2	• Strong breeze. Sky radiation 45° north and east of sun=0.14 μa=.0038 of total at 12:03 p. m.; zenith=0.08 μa at 4.05 p.m. Press. aq. vap.=2.3 mm at 12:45 and 5 p. m. temperature=70° F.
11:53 to 11:59 a.m.	†37.5	†1.04	11.7	1.04	34.1					
2:20 to 2:52 p.m.	†32.1 to *31.0	†1.13	12.6	1.15 1.16	33.7 34.6	1.17	59.3	1.19 *1.21	80.0 80.3	
June 21:										
9:12 to 9:31 a.m.	†26.3 to *28.5	†1.37 1.36	13.4 13.1	1.34	36.2	1.32	58.3	1.31 *1.30	• 80.3 79.7	• Sky clear blue; light wind from west. Press. aq. vap.=2.8 mm; temperature=74° F at 1 p.m.
12:08 p.m.	36.5	1.04								
2:45 to 3:20 p.m.	†29.5 to *26.7	†1.19 1.20	12.4 12.6	1.21 1.23	35.9 36.2	1.25 1.26	61.0 59.7	1.28 *1.30	80.4 81.3	

TABLE 1.—*Filter transmissions of integrated ultraviolet solar radiation for different air masses, m, using a titanium photoelectric cell, Ti No. 4 (see fig. 3)*—Continued

1	2	3	4	5	6	7	8	9	10	11
Date, 1934, and time	Intensity	Ba-3		Ba-1		Ni.		Cx.		Remarks
		m	Tr	*m*	Tr	*m*	Tr	*m*	Tr	
June 22:	μa									
8:51 to 9:58 a.m.	†23.0	†1.47	13.5	1.39	36.2	*1.29	*57.3	1.24	81.0	*See July 6th.
	to	1.41	13.3	1.32	35.6	*1.27	*57.0	1.22	80.7	Sky deep blue; no corona; westerly breeze.
	*30.3	*1.20	12.4	1.31	35.8	1.25	57.2	------	------	Fracto-cumuli suddenly appear at 11 a.m.
										Press. aq. vap. = 3.6 mm.; temperature = 76° F at 11 a.m.
June 26:										
8:55 to 9:40 a.m.	†24.0	†1.46	13.8	1.38	36.7	1.37	58.4	1.33	80.3	
	to	1.43	13.8	------	------	1.35	58.7	1.32	79.5	
	*30.4	*1.26	13.0	------	------	------	------	1.30	79.3	
12:15 to 12:35 p.m.	†37.8	†1.04	11.7	1.04	33.5	1.04	58.2	1.04	79.8	Sky blue; small corona. Light west wind.
		†1.74	16.0	------	------	------	------	------	------	Press. aq. vap. = 2.25 mm; temperature = 76° F at 12:50 p.m.
4:32 to 4:58 p.m.	†18.5	1.79	16.4	------	------	------	------	------	------	
	to	1.85	17.0	------	------	------	------	------	------	
	*14.5	*1.96	16.8	------	------	------	------	------	------	
July 6:										
9:16 to 9:48 a.m.	†24.2	†1.35	12.4	1.32	33.3	*1.29	*57.3	1.26	79.9	*See June 22d.
	to	1.33	12.3	1.30	33.1	*1.27	*57.0	1.25	79.5	Fracto-cirri suddenly appear in west at 10 a.m.
	*28.0	*1.24	11.4	------	------	------	------	------	------	Press. aq. vap. = 5.3 mm; temperature = 79° F at 10:30 a.m.
July 24:										
8:33 to 8:56 a.m.	†20.5 to *23.4	†1.62	15.1	1.60	39.1	1.55	61.0	1.54	81.7	Sky clear, blue after a hard rain.
		*1.47	14.2	------	------	------	------	1.53	81.6	Press. aq. vap. = 4.34 mm; temperature = 81° F at 5 p.m.
3:22 to 3:53 p.m.	†25.5 to *24.3	†1.37	12.9	1.40	35.7	1.44	58.3	1.50	81.3	
								*1.53	81.3	
4:07 to 4:38 p.m.	†22.5 to *17.5	†1.57	14.6	1.63	37.3	1.72	58.5	1.81	81.7	
		------	------	1.69	36.9	1.75	57.8	*1.89	82.0	

July 26:										
12:50 p.m.	34.0	1.04	10.8							Ba-3 transmissions are low. High press. aq. vap.=8.2 mm; temperature=84° F at 1:15 p.m.
July 27:										
7:53 to 8:30 a.m.	†11.4	†2.02	15.2	1.93	39.0	1.84	60.3	1.76	81.3	Sky white, wide corona.
	to	1.98	14.8	1.91	38.8	1.80	60.2	1.71	81.3	Press. aq. vap.=7.85 mm; temperature=81° F at 12:30 p.m.
	*17.5	*1.66	13.2	1.88	38.6	1.78	60.0			
11:32 a.m.	29.8	1.06	10.9							
August 6:										
8:39 to 9:03 a.m.	†18.3	†1.64	15.4	1.51	36.3					Ti No. 4 values are nearly normal; sky is clearer than earlier.
	to	1.61	14.5	*1.50	36.7					Small corona after 9:40 a.m.
	*22.2	1.52	13.7							Press. aq. vap.=9.9 mm; temperature=71° F at 10:50 a.m.
9:43 to 10:04 a.m.	†27.1	†1.30	13.2	1.28	36.4	1.27	58.9	1.25	81.3	
	to	1.29	12.9			1.26	50.0	1.24	80.8	
	*29.5	*1.23	12.8							
August 7:										
8:28 to 9:02 a.m.	†14.6	†1.74	15.2	1.68	40.2	1.62	61.3	1.58	81.2	Sky clear, white around the sun. Light westerly breeze.
	to	1.71	14.9	1.65	39.6	1.61	61.1	1.56	81.8	Fracto-cumulus clouds forming rapidly at 10:15 a.m.; heavy rain in p.m.
	*19.5	1.54	13.6							
		*1.51	13.2							
9:42 to 10:02 a.m.	†24.3	†1.31	12.8	1.29	35.6	1.28	58.6	1.26	81.0	Press. aq. vap.=9.44 mm; temperature=76° F at 10:45 a.m.
	to	1.30	13.0			1.27	58.5	1.25	81.0	
	*26.3	*1.24	12.4							
August 8:										
		2.30	17.7	2.11	43.4	[a]2.04	[a]63.3	†2.40	83.0	Sky clear, small corona. At 8:05 to 8:07 a.m. (m=1.99 to 1.97) sky is whiter.
7:41 to 8:18 a.m.	†8.2	2.26	18.3	2.08	43.2	2.01	63.5	2.36	82.5	[a] See June 9th.
	to	2.22	18.0					2.33	82.4	At 11:20 a.m., very faint haze (smoke) reduces the intensity by 2 to 3 percent.
	*13.8	2.15	17.8					1.99	83.0	
		1.94	16.3	*1.87	42.7			1.97	83.5	
11:16 to 11:31 a.m.	†33.7	†1.10	12.6							Press. aq. vap.=9.3 mm; temperature=75° F at 11:50 a.m.
	to	1.095	12.3							
	*34.5	*1.09	12.1							
August 17:										
8:09 to 8:38 a.m.	†10.5	†2.03	17.4	1.96	42.0	1.89	62.8	1.84	81.5	Wide corona. Sky white; cirri on eastern horizon.
	to	1.98	17.0	1.93	41.9	1.87	62.7	1.81	81.5	Cloudy at 9:30 a.m.
	*14.9	*1.74	15.6							Press. aq. vap.=9.64 mm; temperature =74° F at 10:15 a.m.

TABLE 1.—*Filter transmissions of integrated ultraviolet solar radiation for different air masses, m, using a titanium photoelectric cell, Ti No. 4 (see fig. 3)*—Continued

1	2	3	4	5	6	7	8	9	10	11
Date, 1934, and time	Intensity	Ba-3		Ba-1		Ni.		Cx.		Remarks
		m	Tr	*m*	Tr	*m*	Tr	*m*	Tr	
August 18:	μa									
8:58 to 9:23 a.m.	†17.9	†1.58	14.6	1.55	38.3	1.51	60.0	1.48	80.9	Sky thick, white, clearing slowly, except eastern horizon. "Washington sky." No breeze.
	to	1.57	14.1	1.52	38.2	1.49	60.0	1.47	81.0	
	*21.2	1.46	13.9							* Sky seems whiter southeast of the sun at 10:01 a.m., and transmissions are higher.
		*1.45	13.1							
9:39 to 10:09 a.m.	†22.6	†1.37	13.0	1.35	35.7	1.33	59.0	1.31	81.7	Sky is bluer, clearer, small corona at 9:40 to 10:10 a.m.
	to	1.36	12.9	1.34	36.0	1.32	58.8	1.30	*81.8	Press. aq. vap.=9.2 mm; temperature=79° F at 11:10 a.m.
	*25.6	1.29	12.6	1.33	35.9			*1.27	81.4	
		1.28	12.3							
August 23:										
8:31 to 8:59 a.m.	†12.9	1.72	14.7	1.75	40.2	1.80	61.8	†1.88	83.7	Wide corona; sky pearly white; becoming completely hazy, with fracto-cumulus at 9:45 a.m.
	to	1.70	14.0			1.78	61.6	1.84	82.7	Press. aq. vap.=8.95 mm; temperature=71° F at 10 a.m.
	*17.3	1.66	14.0					*1.63	81.3	
August 27:										
8:14 to 8:24 a.m.	†11.1 to			*2.00	43.0	2.05	63.3	†2.11	84.3	Very unusual sky; thick overcast at 6 a.m.; clear except horizon, from 8 to 8:24 a.m.; suddenly overcast with fracto-cumulus clouds at 8:27 a.m.
	*12.9					2.02	63.5	2.08	83.9	Press. aq. vap.=10.2 mm; temperature=62° F at 8:55 a.m.
September 1:										
9:22 to 9:43 a.m.	†21.1 to	†1.54	13.0	1.49	36.4	1.47	59.3	1.44	81.1	* Fine cirrus clouds over the sun; reduce the intensity nonselectively.
	*24.3	*1.38	12.4					1.42	81.3	
11:27 to 11:46 a.m.	†31.8	†1.15	11.5	1.15	33.3	1.14	56.4	1.13	80.9	Sky clear after several days of rain. Corona small, pearly white.
				1.14	*33.2					Press. aq. vap.=8.67 mm; temperature=72° F at 12:15 p.m.
September 2.										
7:20 to 7:45 a.m.	†2.2	†3.70	20.5	3.25	47.9	3.35	66.7	3.68	83.8	Sky clear at start. Observations stopped by sudden formation of clouds.
	to	3.53	20.2	3.20	47.6	3.30	65.8	3.40	83.6	Press. aq. vap.=6.95 mm; temperature=73° F at 8 a.m.
	*6.1	3.15	19.7			3.27	65.5	3.05	83.0	
		3.10	18.8					*2.90	82.8	

September 3:										
12:05 to 12:30 p.m.	†23.5 to	†1.13	11.3	1.13	* 32.3	1.13	56.3	1.13	80.5	Remarkable day. Sky white; cloudless; smoky, hazy from brush fire or perhaps smelters 30 miles south.
	*22.6	*1.12	11.1							Zenith sky = 0.13 to 0.14 μa; = 0.0058 of total. (See June 20.)
										Press. aq. vap. = 4.6 mm; temperature = 75° F at 12:50 p.m.
September 4:										
8:38 to 9:07 a.m.	†10.8 to	†1.94	15.1	1.87	39.4	1.83	61.3	1.79	83.8	Sky white; air "boils", but cannot see smoke.
		1.73	14.3	1.85	39.2	1.82	60.8	1.77	83.3	* See September 3rd, same air mass. Short wave length ultra-violet is greater than on September 3.
	*12.6	*1.72	14.2							
11:24 to 11:58 a.m.	†29.1 to	†1.15	10.8	1.14	* 32.3	1.14	54.8	1.13	* 80.1	Press. aq. vap. = 5.6 mm; temperature = 76° F at 12:20 p.m.
	*29.6	*1.13	10.6							
September 5:										
										Sky white, clear to horizon; wide corona.
7:37 to 7:56 a.m.	†4.8 to	2.98	19.1	3.03	46.0	3.17	66.7	†3.30	84.0	Sky changing; billowy white streaks 15° east of the sun.
	2.95	18.5	2.98	45.6	3.13	65.5	2.86	82.3	Sometimes definite clouds.	
	*7.7	*2.70	18.1	2.72	44.5	2.77	64.7	2.80	82.5	Sky cloudy; thunderstorm on the San Francisco Peaks at 10:45 a. m.
8:56 to 9:18 a.m.	†16.3 to	†1.80	14.5	1.77	39.2	1.71	60.3	1.69	80.7	Press. aq. vap. = 8.8 mm; temperature 73° F at 9:45 a.m.
	*18.5	*1.63	14.1							
September 7:										
8:15 to 8:37 a.m.	†10.3 to	2.10	16.8	2.14	42.7	2.22	63.5	†2.28	83.8	Sky clear to horizon; corona, pearly white; light, southwesterly breeze.
	*13.2	2.07	16.3			2.19	63.3	*2.04	82.7	Corona narrower; sky clear blue; fracto-cumulus on San Francisco Peaks.
10:05 to 10:28 a.m.	†25.2 to	†1.38	13.5	1.36	36.4	1.35	58.9	1.34	81.5	Sky turning fracto-cumulus clouds at 11:15 a.m.; thunder over the Elden Mountain.
	*27.4	1.33	13.0	*1.31	35.6					
10:45 to 11:02 a.m.	†28.7 to	†1.26	12.6	1.25	34.9	1.24	57.8	1.24	80.2	Sky radiation: Zenith = 0.1 μa; angle 45°, S. W. = 0.12 μa at 10:40 a.m.
	*30.0	*1.23	12.3							Press. aq. vap. = 6.8 mm; temperature = 74° F at 11:25 a.m.
September 11:										
9:25 to 9:50 a.m.	†23.0 to	1.55	13.6	1.59	37.6	1.61	59.8	†1.63	81.7	
	*25.5	*1.50	13.6					1.52	81.7	Sky clear, blue; small corona; light westerly breeze.
11:00 to 11:09 a.m.	†32.3	†1.25	12.3					1.23	81.1	Few clouds on eastern horizon at 9:52 a. m.
11:26 to 11:34 a.m.	*34.2	*1.20	12.0					1.20	80.4	Press. aq. vap. = 5.4 mm; temperature = 73° F at 1 p.m.
11:45 to 11:55 a.m.	*34.8	1.18	11.9					*1.17	80.5	
12:02 to 12:21 p.m.	*35.4	*1.16	11.9	1.16	34.7	1.16	57.3	1.16	80.3	
September 12:										
8:05 to 8:31 a.m.	†10.1	2.38	16.9	2.45	43.4	2.51	64.3	†2.65	82.8	Clouds low on eastern horizon at 8 a. m. Sky deep blue, clearer than yesterday; very small or no corona. Light southwesterly breeze. Clearer than September 7; lower transmissions for larger air mass.
	to	2.31	16.3	2.40	43.2	2.46	63.4	2.54	82.5	
	*14.3					*2.19	62.5	2.24	82.2	
9:23 to 9:58 a.m.	†23.3 to	†1.67	12.4	1.61	33.9	1.59	58.6	1.54	81.5	Press. aq. vap. = 5.3 mm; temperature = 73° F at 12:25 p.m.
11:40 to 11:59 a.m.	*27.5	*1.47	11.8					1.52	81.3	
	40.3							1.19	80.5	

TABLE 1.—*Filter transmissions of integrated ultraviolet solar radiation for different air masses, m, using a titanium photoelectric cell,* Ti *No. 4 (See fig. 3)*—Continued

1	2	3	4	5	6	7	8	9	10	11
Date, 1934, and time	Intensity	Ba-3		Ba-1		Ni.		Cx.		Remarks
		m	Tr	*m*	Tr	*m*	Tr	*m*	Tr	
September 13:	μa									
8:02 to 8:51 a.m.	†7.4	2.15	13.9	2.37	44.2	2.50	64.3	†2.75	83.8	Sky deep blue, small corona at 9 a.m. Sky whiter and corona wider at 10:30 a.m. Corona narrower at 11 a.m.
	to	2.08	13.5	2.28	41.7	2.42	65.7	2.60	82.5	
	*17.1			2.20	41.3	2.38	65.3	*1.99	80.3	
9:46 to 10:31 a.m.	†26.0 to	†1.51	11.9	1.50	36.0	1.43	56.0	1.40	79.5	Sky deep blue, little or no corona at 11:30 a.m. to 12:30 p.m. One of the clearest days of the season. Light northwesterly to westerly breeze.
	*30.8	*1.34	11.3	1.44	35.4	1.42	56.7	1.38	79.7	
11:55 a.m. to 12:21 p.m.	†32.4	†1.16	11.7	1.16	36.1	1.17	56.7	1.18	80.1	Zenith sky radiation=0.07 μa at 10:50 a.m. and 12:20 p.m. Press. aq. vap.=3.38 mm; temperature=72° F at 12:45 p.m.
September 15:		2.40	16.1	2.54	44.3	2.75	66.4	†3.20	88.5	Sky hazy white; wide corona at 7:45 a.m.; narrower at 10:30 a.m. Press. aq. vap.=2.85 mm; temperature=73° F at 11 a.m.
		2.26	15.2	2.49	40.7	2.73	64.5	3.05	86.5	
7:48 to 8:46 a.m.	†5.9 to			2.44	40.7	2.70	64.0	2.90	85.6	
	*14.7			2.41	39.3	2.63	62.5	2.80	83.5	
						2.58	63.8	2.19	82.8	
								*2.10	81.8	
10:26 to 10:36 a.m.	†28.0 to					*1.35	56.0	†1.40	80.5	
	*29.2									

II. CLIMATIC CONDITIONS AT THE OBSERVING STATIONS [3]

During the past year an opportunity was presented to supplement the measurements in progress in Washington (Lat. 38° 56′ N; elevation 350 ft) with similar measurements at the Lowell Observatory, Flagstaff, Ariz. (Lat. 35°12′ N; elevation 7,300 ft); also on the nearby San Francisco Peaks, at an elevation of 10,500 ft; and at the School of Tropical Medicine, San Juan, P. R. (Lat. 18°28′ N; elevation about 75 ft).

At the Flagstaff station successful measurements of ultraviolet solar radiation were obtained under various conditions; high and low humidity, large and small air masses, clear and smoky sky, etc. The data obtained at San Juan are of interest in connection with the question of ultraviolet solar intensities in the tropics.

Incidentally, it is of interest to record climatic conditions during the observations at the three stations. The measurements at Flagstaff, Ariz., were made during the last half of May to the middle of September 1934. This includes a relatively dry, rainless season (May–June) with noon-hour temperatures ranging from 55° F to 75° F, and with pressures of aqueous vapor ranging from 1.6 to 3.6 mm; and a so-called "rainy season" (during July and August), with noon temperatures up to 85° F and pressures of aqueous vapor ranging from 5 to 10 mm.

Weather conditions during the rainy season were fairly regular in sequence, with clear sky during the night and usually until noon or midafternoon, followed by cloudiness (and sometimes rain) clearing again early in the evening, when the cycle was repeated. While this is disconcerting to the meteorologist, it is a boon to the astronomer.

At the Flagstaff station when the wind was from the northwest, the sky was free from smoke. However, when there was a light breeze, the observations were sometimes affected by an almost invisible blue wood smoke (closely matching the blue sky) from a sawmill situated several miles to the south, or by visually imperceptible coal smoke (see fig. 4) from a transcontinental train, some 30 miles to the west. Since the latter disturbance occurred at certain times of the day, no measurements were made at those times.

The ultraviolet measurements at San Juan were made during February and the first half of March 1935. During this time, the forenoon measurements were often interrupted by alternate cloudiness (rapidly moving fracto-cumulus) and sunshine. By noon, and often continuing throughout the entire afternoon, the whole sky was cloudless,—except along the south and southwest horizon, over the inland mountains, where the morning clouds (now cumulus and strato-cumulus) had been blown by the prevailing north and northeast winds.

The School of Tropical Medicine being situated on the north shore of the island, the observing station was free from smoke from ships in the harbor, close by to the south, and from burning refuse of harvested sugarcane on the plantations still farther to the south.

[3] The observations of the effect of altitude at Flagstaff, Ariz., were obtained with grants from the Council on Physical Therapy of the American Medical Association and from the American Academy of Arts and Sciences. The measurements on the effect of latitude were obtained in connection with the standardization of ultraviolet meters at the School of Tropical Medicine, San Juan, P. R., under the auspices of Columbia University.

While there are numerous, perfectly cloudless days, which occur at irregular intervals during the year, no characteristic, long-continued, cyclical, regularly recurring, clear-weather conditions can be described for the Washington station. Situated on high ground in the northwest part of the city, and gradually being surrounded by residences, high-precision ultraviolet observations for standardization purposes are made only on the clearest days. These usually occur when the wind is from the northwest or west, especially after a hard rain, when the air over the southeastern part of the city (through which the forenoon measurements must be made, especially during the winter months) is relatively free from pollution by smoke and dust. The ultraviolet measurements made under various meteorological conditions are of statistical interest indicating the amount of ultraviolet available in a city relatively free from factory smoke.

III. MINOR OBSERVATIONS

In addition to the prolonged measurements of the effect of solar altitude (air mass), and of the geographic latitude and the altitude of the observing station, similar observations, of short duration, were made of the effect of numerous local meteorological conditions upon the spectral quality and total intensity of ultraviolet solar radiation

For example, the effect of smoke from burning coal or wood is to reduce the total intensity, and to increase the percentage transmission of the filters, indicating a highly selective absorption of the short wavelength ultraviolet solar rays. That this is not always true is shown by measurements through a peculiar thin smoke of undetermined origin (whether of forest fire or smelters) that suddenly enveloped the Flagstaff station for a day (September 3, 1934, sky cloudless, white, no distinct corona). While this reduced the total ultraviolet intensity by almost 35 percent (see fig. 4) the transmissions of ultraviolet through the filters remained unchanged and in agreement with the values prevailing at that season, suggesting a uniform ("gray") absorption throughout this spectral region.

At unexpected times (July 30, 1934; a hot day; ozone should be low) the filter transmissions were lower (the Ba–3 filter transmissions remained fairly constant, amounting to 11.3 to 11.5 percent, between 9:30 and 10 a. m.—$m=1.30$ to $m=1.23$) than the prevailing values for a given air mass, observed at the Flagstaff station at that season of the year. This could not be accounted for on the basis of observational errors or unclean filters. A more plausible explanation is that there was either an increase in atmospheric transparency, caused by a temporary decrease in the amount of ozone in the stratosphere, or a temporary increase in emission of short wavelength ultraviolet solar radiation. Similarly, as will be more fully described on a subsequent page, on January 24, 1935, which was an exceedingly clear day in Washington, the filter transmissions were unusually high (fig. 7) whereas, on the basis of a clear sky, free from local atmospheric pollution, there should have been an increase in intensity of ultraviolet, of the shortest wave lengths, hence the filter transmissions should have been lower. Apparently, the high transmissions were owing to an unseasonably high ozone content (equivalent to a layer of the pure gas, 3 mm in thickness at normal temperature and pressure, ntp; see fig. 7).

Thin, cirrus clouds over the sun which reduced the intensity by several percent, did not appreciably affect the spectral qualities indicated by the filter transmissions. The effect of high humidity (as indicated by a pearly white corona) on ultraviolet absorption is not marked through a small air mass, but is observable through a large air mass.

The sea-level observations indicate that the short wave length ultraviolet solar spectral energy curve is constantly changing as the result of variations in atmospheric pollution. Hence, where great refinements are required, no standard ultraviolet solar spectral energy curve can be assumed for a given air mass.

On exceptionally clear days in Washington, and especially at the higher elevations, the measurements are consistent in showing a higher atmospheric transparency to ultraviolet, for the same solar altitudes, in the afternoon than in the forenoon (fig. 5), which is explained on the basis of a decreased ozone content, principally by thermal decomposition (4).

In agreement with expectations, the transmission of ultraviolet solar radiation through the various filters increases with increase in air mass. At the Flagstaff station atmospheric conditions were so constant (see fig. 4) that a definite change in transmission was observable in the course of a few minutes, corresponding with a small change in air mass, amounting to only $\Delta m=0.02$.

1. FOG

Interesting ultraviolet measurements were made through a light fog of short duration in Washington, at 2:30 p. m., January 21, 1935. When the fog was fairly homogeneous, the sun's disk appeared white, and the integrated ultraviolet intensities were less than 10 percent as great as observed during clear weather through a similar air mass, $m=2.5$. When the fog began to form into clouds the ultraviolet intensities increased to one-fifth the clear weather values. In both cases, within the errors of observation, the average values of the filter transmissions were closely the same as observed during clear skies, with the sun shining through the same air mass, indicating that the fog particles (water vapor) exerted but little selective absorption upon the transmitted ultraviolet rays.

2. SNOW

It is well known that snow is a strong reflector of ultraviolet rays. Measurements (5) on July 28, 1932, on the Jungfraujoch, (elevation 11,350 ft), using a wide-angle receiver indicated that the ultraviolet reflected from snow was almost as intense as that of direct solar radiation.

The Jungfraujoch observing station is situated on one mountain side and faces a similar, steeply inclined, close-by mountain side, with the intervening valley covered with glacial ice and snow. Hence it is an excellent location for the measurement of ultraviolet sky and direct solar radiation, through light fog and falling snow. All measurements (5) show a high intensity of ultraviolet through fine mist and snow particles.

3. SKY

Ultraviolet radiation from the sky is indefinable without a specification of atmospheric conditions. It has been mentioned repeatedly by other observers. Using a wide-angled receiver, on the Jungfraujoch (5) with the sun obscured by mist or fine particles of falling snow, the ultraviolet intensity was almost one-half that of direct sunlight, in a cloudless sky. At the Flagstaff station, using an aperture of 22°, with a cloudless, deep-blue sky, showing practically no corona, the ultraviolet sky radiation at an angle of 45° from the sun at the noon hour, was only 0.38 percent as great as direct solar radiation. When the atmosphere was hazy, smoky (e. g., September 3, above mentioned, when the direct ultraviolet solar intensity was reduced by one-third) the sky radiation was 0.58 percent as great as direct ultraviolet solar radiation, or 65 percent greater than during the clearest weather. (See table 1, data for June 20 and September 3, 1934.)

Sky radiation is most pronounced at sea-level stations. Using a receiver with a wide aperture (45°) at Washington, (6) the ultraviolet sky radiation in a 45° angle directly surrounding the sun, amounted to about 7 percent of the total incident solar ultraviolet, under average atmospheric conditions; rising to 19 percent of the total measured when the sky was turbid from a forest fire, the smoke of which reduced the intensity of the directly incident solar ultraviolet to almost one-third the value observed through a clear sky.

Atmospheric pollution by dust, transported long distances, as experienced in Washington in March–April 1934 and 1935, appears to have only a very temporary effect upon ultraviolet transmission and is entirely different from the prolonged effect of dust that is blown to high altitudes, by volcanic eruptions, such as, for example, the eruption of Krakatoa, which is often cited with reference to the effect of atmospheric dust upon meteorological conditions.

For example, the ultraviolet solar intensities, for $m=1.20$, as measured with the standard ultraviolet meter (using Ti No. 4) on May 7, 1934, and May 18, 1935, differed by less than 6 percent; also, the transmissions of the filters (Tr. of Cx.–D=80.8 and 81.1 percent, respectively) showed no difference in the spectral quality of the solar ultraviolet on these two dates, from which it appears that the dust had been removed by heavy rains. This, of course, was apparent also from visual observations of atmospheric turbidity.

4. ERYTHEMA TESTS

In a previous communication (17) data were given on the time of exposure (the total ultraviolet solar energy) required to produce a minimum perceptible erythema. In that paper it was shown that an exposure of 20 to 30 minutes to a midsummer noonday sun is required to produce a minimum perceptible erythema. It was also shown that to produce a minimum perceptible erythema, in the winter when the skin is dry, about twice as much energy (twice the time of exposure using standard wave length 2967 A) is required as in the summer, when the skin is moist.

In the above-mentioned tests (17), before exposure to heterogeneous ultraviolet radiation the skin-sensibility was standardized by exposure

to homogeneous radiation of wave length 2967 A, of known energy value. Such a preliminary standardization was not practicable before making the erythema tests outside of Washington. Hence only general statements regarding erythemogenic action can be made.

The erythema test at the Lowell Observatory station (elevation 7,300 ft) was made early in the afternoon (1:08 to 1:22 p.m.; air mass, m=1.04 to 1.08) on a cloudless day (June 10, 1934). The temperature was 76° F, and the vapor pressure was down to 1.58 mm. It is therefore presumed that the skin was dry, requiring a longer exposure to produce a minimum perceptible erythema than if the skin had been moist from perspiration, which occurs during exposure to the sun.

Small areas of the left upper inside arm were exposed for intervals of 2, 5, 7, 9, 10, 12, and 14 minutes, respectively. The exposures of 12 and 14 minutes, respectively, evidently were too long—the skin being sensitive to the clothing worn. On the evening of June 11, the four longest exposures appeared lightly pigmented; and a week later (June 17) they were still visible being pigmented dark brown. The time of exposure to produce a minimum perceptible erythema appeared to be between 9 and 10 minutes or about one-third (to one-half) the time for a low-level exposure.

During the erythema tests at the San Juan station the exposures (made through an air mass m=1.1, March 11, 1935) were interrupted by passing clouds. A minimum perceptible erythema was produced by an exposure of 21 to 22 minutes, which is not markedly shorter than observed on a moist skin, exposed at Washington. The most important observation was that the shortest exposures (of 14 and 18 minutes; utilizing about 450,000 to 600,000 ergs of ultraviolet radiation) showed no erythema, but after several days showed slight pigmentation which continued to be visible for several weeks. To what extent this is caused by the humid sea air is unknown.

It is important to note that tanning is caused not only by wave lengths (including, and shorter than, 3130 A) that produce an erythema but also by wave lengths between 3200 to 3300 A that have little or no power to produce an erythema; also that the tanning resulting from long exposure at the San Juan station was a characteristic light brown, as distinguished from the dark brown obtained at the Flagstaff and Washington stations.

The present measurements substantiate the earlier data (5) showing that the greater susceptibility to sunburn at the seashore is not explainable exclusively on the basis of an excessively higher ultraviolet radiation than obtains at the same level inland; but that skin sensitization by sea water, and increased penetrability of the rays into the moist skin must also be considered.

IV. EFFECT OF ALTITUDE ON ULTRAVIOLET SOLAR RADIATION

As already mentioned, by using a selective radiometer that responds only to the ultraviolet of wave lengths shorter than about 3300 A, and a group of 4 glass filters, it is possible to analyze the everchanging spectral quality and total intensity of radiation in this narrow band (about 400 A in width) of ultraviolet in sunlight, apparently with as high degree of reliability as anything yet attained by means of spectral radiometry.

The results of these measurements corroborate what was already known in a general way, that ozone, which has a high absorption in the ultraviolet (2200 to 3200 A) and is situated in greatest abundance in the stratosphere, at an average height of 21 to 24 km, depending upon the station (9), (10), (11), determines the spectral quality of ultraviolet radiation incident upon the earth's surface. Water, in the vapor state, as it ordinarily exists in the atmosphere, and as observed in a light fog, appears to be relatively nonselective in spectral ultraviolet transmission, the loss in intensity being caused by scattering, principally by reflection within the particles of water.

The amount of ultraviolet reaching the earth's surface is controlled by ozone in the stratosphere and by atmospheric pollution, by dust and smoke, near the surface. The chief gain in ultraviolet intensity and, to a less degree, in spectral quality, appears to result from rising above the first 7,000 ft (2 km) elevation above sea level, in which occurs local pollution by smoke and dust. To eliminate a large amount of the ultraviolet absorption by ozone would require an elevation so great that it would be impracticable for large-scale physiological and biological tests.

By means of ultraviolet filter transmission measurements, at high elevations, it is possible to observe small variations in the transparency of the upper atmosphere that are masked or rendered doubtful by rapid changes in local pollution when similar measurements are made at low elevations.

Outstanding among the measurements made at Flagstaff, Ariz., is the observation of a lower filter transmission, indicating a higher atmospheric transparency and a consequent greater amount of incident ultraviolet of the shortest wave lengths, for the same air mass, in the afternoon than in the forenoon (fig. 5). A good example is a set of measurements made on June 26, 1934, using Ti No. 1 photoelectric cell and the Ba.–3 filter. At 9:53 a.m. (m=1.21) the transmission of this filter was 25.7 percent and at 2:54 p.m. (m=1.21) it transmitted 24.8 percent.

This greater atmospheric transparency in the afternoon than in the forenoon was especially noticeable during the dry season, in May-June, with the sky cloudless to the horizcn throughout the day (and night) when, judged by the size of the corona (if any was visible) surrounding the sun, there appeared to be no visual difference in (a.m. and p.m.) atmospheric conditions, for the same solar altitude. The marked difference in solar altitude for the same filter transmission (e. g., air mass m=1.25 in the a.m. and m=1.40 in the p.m. in June) seems sufficient to be unmistakable in indicating a greater atmospheric transparency in the afternoon. Similarly the observations show a higher transparency in the autumn than in the spring—a phenomenon previously observed by others (7), (8), by means of spectrographic measurements of ultraviolet intensities at different solar altitudes.

In this connection it is to be noted that pollution of the air by smoke (from the above-noted railroad engine) in the afternoon, would have selectively absorbed the ultraviolet of short wavelengths and, hence, increased the filter transmissions. This difference in atmospheric transparency from forenoon to afternoon is, therefore, to be ascribed to variations in the amount of ozone in the stratosphere. From the

data given in figures 5 and 7 it is estimated that the observed decrease in ozone amounted to 0.1 mm (ntp).

An explanation, by Kidson (4), to account for the presence and variability of ozone, is based primarily upon a photochemical reaction caused by short wave length ultraviolet solar radiation. Among other causes, radiation of wave lengths shorter than 1850 A, acting upon oxygen in the uppermost atmosphere, produces ozone which in turn is subjected to decomposition by heat and by solar radiation of wave lengths 2200 A to 3300 A. In this manner an equilibrium in photochemical action is established, which is a function of the ultraviolet solar intensity, and the temperature of the upper atmosphere.

This accounts for the relatively constant amount of ozone in the tropics and the annual variations in the higher latitudes, where the amount of ozone is a maximum in the local spring and a minimum in

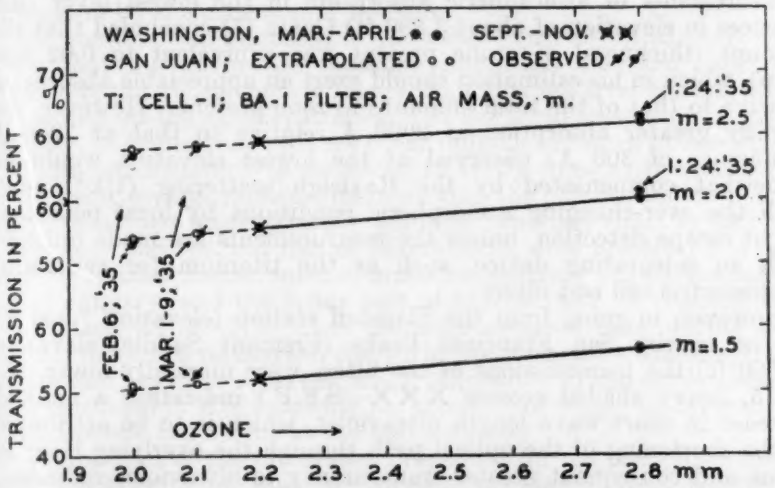

FIG. 7.—*Filter transmissions of ultraviolet solar radiation after passing through various air masses containing different amounts of ozone.*

the local autumn. In addition to these variations, Dobson and Meetham (12) report marked daily variations in the total amount of ozone (in Europe) with varying meteorological conditions; the maximum amounts being generally observed with cyclones and the reverse with anticyclones. In view of these facts a more complete study of the data obtained at Flagstaff in July 1934, in connection with the barometric pressures at that time may perhaps disclose the reason for the low filter transmissions (apparent low ozone content and high ultraviolet intensities) observed at that time.

From the measurements obtained with the titanium photoelectric cells and filters, and from the earlier, less extensive spectral-energy data, it appears that, for a given solar altitude (say air mass, $m=2.0$), at sea level (Washington) the relative spectral-energy distribution, of the solar radiation shining through an atmosphere free from local pollution, is closely the same (at least in the small spectral range of 2900 to 3300 A) as that observed at a much higher elevation (Flagstaff, Ariz., altitude 7,300 ft) for an appreciably lower solar altitude (larger apparent local air mass, $m=2.4$).

The spectral-energy data obtained with a spectroradiometer, by Greider and Downs (13) at two stations differing widely in altitude (at Springfield Lake, Ohio and Colorado Springs, Colo.) support these observations showing that, while the total intensities differ appreciably, within the experimental errors in making the observations, there is no marked difference in the shape of the spectral-energy distribution in this narrow spectral range for equivalent air masses, at these two stations.

The foregoing observations are to be expected, owing to the fact that the shape of the part of the solar spectral-energy curve in the region of 2900 A to 3200 A is determined largely by a layer of ozone, which has a strong absorption band that extends from about 2200 A to 3200 A, with a maximum at about 2530 A. The average amount of ozone [4] in this layer is equivalent to about 3 mm (ntp). From his measurements of atmospheric absorption in the lowest layer (differences in elevation of about 3,800 ft) Goetz (7) concluded that the amount (thickness) of ozone present was equivalent to 0.02 mm (ntp), which in his estimation should exert an appreciable absorption relative to that of the total amount of ozone present. However, the slightly greater absorption at 2900 A relative to that at 3200 A (difference of 300 A) observed at the lowest elevation would be somewhat compensated by the Rayleigh scattering ($1/\lambda^4$), and, with the ever-changing atmospheric conditions by local pollution, might escape detection, unless the measurements are made quickly, with an integrating device, such as the titanium (or cadmium) photoelectric cell and filters.

However, in going from the Flagstaff station (elevation 7,300 ft) to the nearby San Francisco Peaks (Fremont Saddle, elevation 10,500 ft) the transmissions of the filters were markedly lower (see fig. 5, heavy shaded crosses XXX—S.F.P.) indicating a marked increase in short wave length ultraviolet, which is to be attributed to the shortening of the optical path through the overlying layer of ozone and consequent greater transparency to ultraviolet radiation. Measurements at the higher elevation (Fremont Saddle, elevation 10,500 ft) were made during midday on June 12 and July 5, 1934, under fairly clear atmospheric conditions. The total ultraviolet intensity, as measured with Ti No. 4, was 18 percent higher on June 12, and 15 percent higher on July 5, than observed under similar conditions at the Lowell Observatory station (elevation 7,300 ft).

Further evidence of greater atmospheric transparency in the fall as compared with early summer, is shown in figure 4, where the intensities for June 7 and September 11, for air mass $m=1.25$ are connected with a dotted line. The value for September 11 is about 7 percent higher—4.5 percent higher after correction for difference in solar distance. The intensities at the noon hour, on those two dates are closely the same in spite of the differences in solar altitude—$m=1.04$ and 1.16, respectively. It is relevant to add, that the air masses (solar altitudes) are so closely the same during the first part of June that no attempt was made to plot the intensities relative to solar altitude instead of the time of the day.

[4] Dobson (8) found that over continental Europe the atmospheric ozone varies in a seasonal cycle ranging from a maximum of about 3.3 mm (ntp) in April to 2.3 mm in October. Goetz cites variations between 1.7 mm and 4.2 mm. Regner (9) found 70 percent of the ozone below 30 km.

V. EFFECT OF GEOGRAPHIC LATITUDE ON ULTRAVIOLET SOLAR RADIATION

Measurements of ultraviolet solar radiation intensities in the tropics, particularly near the seashore, are of interest because of a vaguely defined belief that the sea air imparts some peculiar physiological property to these rays.

The intensity of the ultraviolet rays reaching the earth's surface is determined principally by the amount absorbed by the ozone in the stratosphere, and only to a minor extent by absorption in the lower atmosphere. The lower stratum of air, over the ocean, cannot restore the ultraviolet absorbed in the upper atmosphere. The higher ultraviolet intensity, if any, at the seashore, as compared with an inland sea-level station, is owing to a greater atmospheric transparency, caused by a greater freedom from dust and smoke, which is determined by the direction of the wind.

This question was discussed in an earlier paper (5) in which it was shown that the ultraviolet radiation intensities observed over the ocean were not conspicuously higher than at a sea-level station, situated inland, at the same latitude and at the same season of the year. Recently, in connection with the other radiometric work at San Juan, P. R., an opportunity was presented to verify these earlier measurements, using greater refinements in making the observations.

The ultraviolet measurements, made in San Juan (Lat. 18°28′ N.) in February and the first half of March 1935, were preceded and followed by similar measurements, made respectively during the latter part of January, and the latter part of March 1935, at Washington, D. C. (Lat. 38°56′ N). It is therefore assumed that, during this interval, there was no marked change in the ultraviolet emission from the sun and that the observed small differences in ultraviolet intensities, discussed in the following paragraph, are owing to differences in atmospheric conditions at the two stations.

A comparison of the ultraviolet intensities for the same air masses (m) at the Washington and the San Juan stations, shows a difference of 10 percent for $m=2$ and 7 percent for $m=1.5$ in favor of the San Juan station. While this small difference in ultraviolet intensity may be attributed to greater local air pollution by dust and smoke at the inland, Washington station, it is more likely to be owing to the greater amount of atmospheric ozone in the higher latitude, as indicated by the greater difference in intensities at air mass, $m=2$, as compared with $m=1.5$.

Interesting measurements were made on January 24, 1935, which was an exceedingly clear day, with a noon-hour temperature of 12° F., with snow on the ground and with the trees covered with ice. The total solar intensity was $Q=1.47$ g cal per cm^2 per minute, the highest seasonal record, in years, in Washington. This high total radiation intensity is accounted for on the basis of a low pressure of aqueous vapor, which is very opaque to infrared rays and, hence, is most effective in summer.

The ultraviolet filter transmissions were unseasonably high, corresponding with a high ozone content (equivalent to a layer of the pure gas, 3 mm in thickness, at normal temperature and pressure (ntp), see fig. 7) such as might be expected if the prevailing low temperature was instrumental in conserving the ozone. Incidentally it

is to be noted that since atmospheric ozone reduces the total incident solar radiation by only 1 part in 1,000, a slight increase in ozone, which greatly affects the ultraviolet at 2900 to 3200 A, has but little effect upon the total solar intensity. Hence there is nothing inconsistent in our observation of a relatively low ultraviolet intensity and the Weather Bureau measurement of a high total intensity on January 24, 1935.

The filter transmission measurements made at San Juan, especially during the first part of February, are definitely lower for the same air mass than in Washington, indicating a greater intensity of short wave length ultraviolet in the tropics. This is to be ascribed to a smaller amount of ozone in the tropical atmosphere (figs. 7 and 8).

In this connection it is of interest to record that on the basis of published data (14) giving the local seasonal amount of ozone present at different latitudes, the atmospheric ozone at Washington is a minimum (thickness of layer equivalent to about 2.2 mm, ntp) in September–October and a maximum (about 2.8 mm, ntp) in February–March–April. On this basis the ozone at San Juan would amount to about 2.0 mm (ntp) in January–February, rising to 2.1 to 2.2 mm (ntp) by the middle of March.

Plotting as ordinates the transmission data, for a given filter (e. g., Ba–1), observed at Washington, at a particular air mass (m= 1.5; also m=2.0 and m=2.5), at the two above-mentioned seasons; and plotting as abscissas the corresponding amounts of ozone at these two seasons, and extrapolating these transmission curves (for different air-masses, m=1.5, 2.0, 2.5) to an ozone content of 2.0, gives the percentage transmission to be expected at San Juan—the circles, ○○○, in figure 7. It is interesting to record that the percentage transmission of the filters, observed during the first part of February, are in very close agreement with the predicted values, for an ozone content of 1.9 to 2.0 mm, (equivalent thickness (ntp))—figure 7. Moreover, as the season advanced the average values of the transmissions of the filters became unmistakably higher (see fig. 8) particularly by the middle of March, in agreement with the expected seasonal increase in the amount of ozone (2.1 to 2.2 mm) in the tropics, and corresponding with the Washington transmissions, observed in September–October, when the estimated amount of ozone is equivalent to a thickness of about 2.2 mm (ntp).

From the fact that there is less ozone in the atmosphere in the tropics than at higher latitudes, and from the above-mentioned differences in the direct measurements of solar intensities at the two stations, it appears that, for the same solar altitude (air mass traversed) the intensity of short wave length ultraviolet solar radiation is slightly greater at a sea-level station in the tropics than at a similar station in higher altitudes.

However the slight difference in spectral quality and total intensity of ultraviolet solar radiation, for the same solar altitude in the tropics and at higher latitudes, is not the only factor to be considered in connection with differences in physiological effects (e. g., practically no rickets in the tropics) that are observed in different latitudes.

For, in addition to differences in air movement, temperature, humidity, amount of clothing worn, and hours of sunshine per year, it is to be noted that in midlatitude (Washington) during only 2 months of the year (May 15 to July 15) does the sun shine through an

atmosphere of air-mass, $m=1.04$ to $m=1.05$ (never less than $m=1.04$) at the noon hour, whereas in the tropics (San Juan) during almost 6 months, at the noon-hour the sun shines through an air mass of $m=1.05$ or less. Twice during this interval (about May 12 and about August 1, at San Juan) the sun is in the zenith, $m=1.0$; and during an interval of about 4 months (April 20 to August 20) at the noon hour the sun shines through an air mass of $m=1.00$ to 1.01. Consequently during this period not only is the spectrum richer in the shortest wave lengths, but also the total intensity of the short wave length ultraviolet solar radiation at San Juan, at the noon hour, is about 15 percent higher than for air-mass $m=1.05$, or (owing to the latitude effect), about 20 percent higher than is ever attained in Washington—a phenomenon that can occur at a sea-level station only in the tropics. In higher latitudes it is necessary to ascend to high elevations to attain

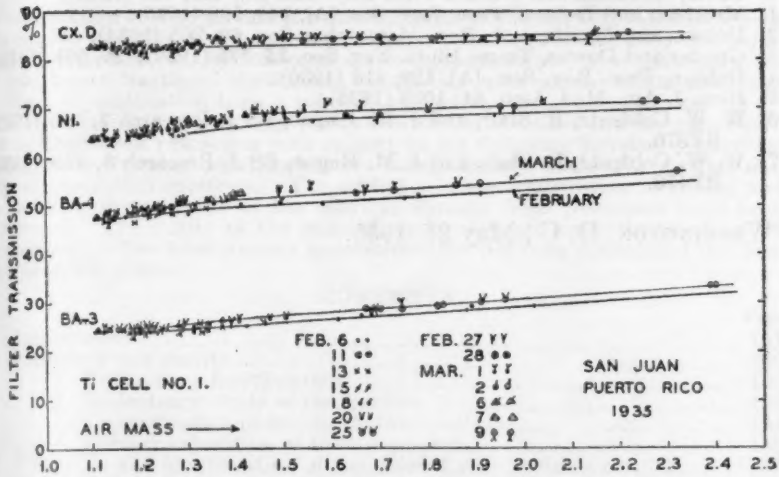

FIG. 8.—*Diurnal variation in transmission of ultraviolet solar radiation through standard filters (see fig. 3), observed at San Juan, P. R.*

this increase in intensity. At the Flagstaff station, for $m=1.05$ the ultraviolet intensities were 40 to 50 percent higher than at Washington.

It is equally interesting to compare ultraviolet intensities during the winter months. At the winter solstice (Dec. 21) the maximum air mass traversed by the solar rays, at the noon hour, is $m=1.34$ at San Juan and $m=2.1$ at Washington. Between October 1 and March 15, the air mass traversed by the solar rays at the noon-hour, at Washington, is always greater than $m=1.34$ and increases to $m=2.1$ in December, at which time the intensity is about one-sixth the value that obtains when $m=1.34$ and only about one-tenth the summer value when $m=1.04$.

From this it can be seen that in the 5 winter months, when the short wave-length ultraviolet in sunlight is most needed in preventing rickets, the shortest and most effective wave lengths are almost completely absorbed at a midlatitude station (Washington) and the intensity of the less effective wave lengths is less than one-sixth the value that obtains in the tropics. In addition to this fact the actual number of hours of sunshine must be considered (15)—ranging (in the

5 winter months) from a total of about 200 hours in London and Stockholm, 300 to 350 hours in Berlin and Paris, 800 hours in New York and Colon, and 1,100 hours in San Juan.

VI. REFERENCES

(1) W. W. Coblentz and R. Stair, BS J. Research **12**, 231 (1934) RP647.
(2) Pettit, Astrophys. J. **75**, 195 (1932).
(3) Fabry and Buisson, Astrophys. J. **54**, 297 (1921).
(4) Kidson, Proc. Roy. Soc. [A] **129**, 421 (1930).
(5) W. W. Coblentz, R. Stair, and J. M. Hogue, BS J. Research **10**, 79 (1933) RP517.
(6) W. W. Coblentz, R. Stair, and J. M. Hogue, BS J. Research **6**, 951 (1931) RP318.
(7) Goetz and Ladenburg, Naturwissenschaften, **19**, 373 (1931).
(8) Dobson and Harrison, Proc. Roy. Soc. [A], **110**, 660 (1926).
(9) Regener, Phys. Z. **35**, 788 (1934).
(10) Goetz, Meetham and Dobson Proc. Roy. Soc. [A], **145**, 416 (1935).
(11) Meetham and Dobson, Proc. Roy. Soc. [A], **148**, 598 (1935).
(12) Dobson and Meetham, J. Roy. Meteorolog. Soc. **60**, 265 (1934).
(13) Greider and Downs, Trans. Illum. Eng. Soc. **25**, 378 (1930); **26**, 561 (1931).
(14) Dobson, Proc. Roy. Soc., [A], **129**, 418 (1930).
(15) Hess, J. Am. Med. Assn. **84**, 1033 (1925).
(16) W. W. Coblentz, R. Stair, and J. M. Hogue, BS J. Research **7**, 723 (1931) RP370.
(17) W. W. Coblentz, R. Stair, and J. M. Hogue, BS J. Research **8**, 759 (1932) RP450.

WASHINGTON, D. C., May 25, 1935.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP817

Part of Journal of Research of the National Bureau of Standards, Volume 15, August 1935

ISOLATION OF ETHYLCYCLOHEXANE FROM A MIDCONTINENT PETROLEUM[1]

By Frank W. Rose, Jr.,[2] and Joseph D. White[2]

ABSTRACT

Fractionation of that portion of a midcontinent petroleum which normally boils between 131 and 133° C has resulted in the isolation for the first time of a naphthene identified as ethylcyclohexane. The methods employed in its separation are systematic fractional distillation, distillation with glacial acetic acid, and fractional crystallization from a solution in liquid propane and methane.

Ethylcyclohexane of very high purity has been synthesized and compared with that isolated from petroleum with respect to the following physical properties: Boiling point, freezing point, refractive index, density, molecular weight, and infrared absorption spectrum. The critical solution temperature in aniline and the carbon-hydrogen ratio of the ethylcyclohexane from petroleum have been determined. The purity of the isolated material is estimated to be about 95 mole percent. The total content in petroleum has not been determined but does not exceed 0.1 percent.

CONTENTS

	Page
I. Introduction	151
II. Procedure and results	152
1. Preliminary fractionation	152
2. Preliminary study of the fraction	153
3. Crystallization of the distillation fractions	154
4. Further separation of the component	155
III. Properties and identification of the isolated ethylcyclohexane	157
1. Preparation and purification of the synthetic hydrocarbon	157
2. Properites of the material isolated from petroleum	157

I. INTRODUCTION

In the literature concerning the composition of petroleum one finds the occurrence of many hydrocarbons established by speculation rather than by isolation. Thus, the only reported suspicion of the presence of ethylcyclohexane in petroleum is based on trends in certain physical properties of a distillate. In an investigation of Roumanian petroleum freed of aromatic hydrocarbons, Poni,[3] after repeatedly distilling the oil in a fractionating column, observed slight maxima at 132 to 134° C in the curves obtained by plotting the volumes and densities of the fractions against their boiling points. He inferred the presence of ethylcyclohexane from these maxima.

In the present work, no evidence[4] of a compound boiling at 131 to 132° C was apparent after a preliminary distillation, an extraction

[1] Financial assistance for this work has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research Associate at the National Bureau of Standards, representing the American Petroleum Institute.

[3] P. Poni, Ann. Scient. de l'Univ. de Jassy, **2**, 74 (1903).

[4] J. D. White and F. W. Rose, Jr., BS J. Research **9**, 712 (1932) RP501. See figure 1, graph II.

to remove the bulk of the aromatic constituents, and a subsequent systematic distillation in a 30-plate fractionating column. However, with continued redistillation, latterly in more efficient columns, concentration of a naphthene was noted.

The fraction of oil boiling normally from 131 to 133° C, upon extended application of physical methods of separation, yielded the naphthene, ethylcyclohexane.

II. PROCEDURE AND RESULTS

1. PRELIMINARY FRACTIONATION

The source of the petroleum for this investigation has been described elsewhere.[6] Under the direction of S. T. Schicktanz the naphtha fraction had been subjected to 6 systematic distillations (3 at atmospheric pressure followed by 3 at 215 mm Hg). The distillations were carried out in Pyrex glass bubblejcap columns, using a reflux ratio of 10:1 and a rate of about 1 ml per minute, collecting the distillate in 0.5° cuts. After the first and second distillations, the material had been extracted with liquid sulphur dioxide to remove the bulk of the aromatic hydrocarbons.

The distribution of volume with boiling point at the end of the sixth systematic distillation has been shown in an earlier paper.[6] Cuts having boiling points below 90° C at 215 mm Hg (132° C at 760 mm Hg) had been combined with cuts of the same boiling point obtained as a result of distilling mother liquors from the crystallization of *n*-octane.[7] The combined material had been systematically distilled once at atmospheric pressure and again extracted with liquid sulphur dioxide. The immiscible portion, together with the fractions boiling normally at 132 to 133° C, had been treated with concentrated sulphuric acid, and redistilled at atmospheric pressure. Meanwhile, the use of more efficient columns packed with jeweler's locket chain to distil fractions containing isononanes (boiling point ca. 135° C) had resulted in the separation of a portion of that stock as a lower-boiling fraction.

A graph showing the boiling-point—volume and boiling-point—refractive-index relations of all the distillates accumulating in the range 129 to 135° C, is given in figure 1. The salient features of the data illustrated are: (1) the volume maximum occurring at 131.5° C; (2) the proximity of this volume maximum to that of the refractive index. Hence, it may be concluded that one or more compounds, naphthenic in nature, are the major constituents in this range. The total volume of oil distilling in the interval 129.5 to 134.5° C amounts to only 5.5 liters, approximately 75 percent of which is naphthenic. It may be noted that this is from 600 gallons of the original crude oil. The broadness of the peak, together with the theoretical possibility of several octonaphthenes boiling in this range having either cyclopentane or cyclohexane rings, points to the presence of more than one hydrocarbon.

[6] E. W. Washburn, J. H. Bruun, and M. M. Hicks, BS J. Research 2, 469 (1929) RP45.
[6] J. D. White and F. W. Rose, J. Research NBS 13, 801 (1934) RP745, figure 2.
[7] R. T. Leslie and S. T. Schicktanz, BS J. Research 6, 377-386 (1931) RP282.

2. PRELIMINARY STUDY OF THE FRACTION

Inasmuch as the larger of two portions comprising the available oil of this range had not been distilled in the more efficient locket-chain columns, this material, together with appropriate fractions resulting from the isononane distillation, was given such a fractionation. Owing to the paucity of material, extensive combination of fractions having the same boiling point and refractive index was often necessary to produce charges of sufficient size. As a result of this distillation, there was separated approximately 1,800 ml of

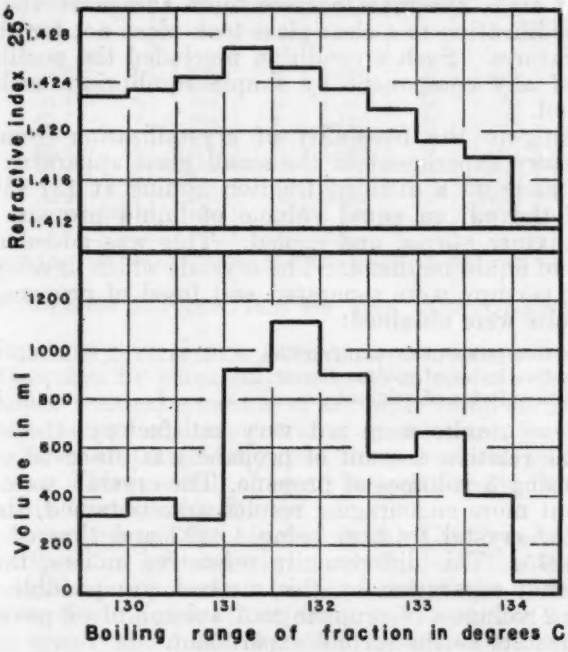

FIGURE 1.—*Volume distribution and refractive indices with respect to boiling range (760 mm Hg) at start of work.*

oil boiling principally at 131.8° C, and having a refractive index of 1.4275,[8] but covering the range of 131.5 to 132.5° C in boiling point and 1.4265 to 1.4285 in refractive index.

To ascertain whether all aromatics had been removed by the concentrated sulfuric acid, a sample fraction was treated with the usual nitrating acid.[9] So much heat was generated that cooling was necessary and nitrous fumes were evolved. The unattacked oil was neutralized and distilled from sodium. The acid layer gave a reddish-brown oil when poured upon ice. This is possibly indicative of ethylbenzene. The effect of the nitration on the refractive index was as follows:

Original oil	1.4285
Oil after treatment	1.4277
Reduction by nitration	.0008

[8] All refractive indices in this paper are for n_D^{25} unless otherwise noted.
[9] J. H. Bruun, R. T. Leslie, and S. T. Schicktanz, BS J. Research 6, 364 (1931) RP280.

In view of the oxidation shown by the presence of nitrous fumes, the change in refractive index could be attributed to the decomposition of the naphthene. If it is due to the removal of aromatics, a concentration of about 2 mole percent of the latter is indicated. It was deemed inadvisable to attempt to remove these small residual amounts of aromatics by nitration owing to the vigor of the reaction and to the possibility of serious loss of the naphthene.

A selected fraction of the oil, having a refractive index of 1.4270 and a boiling point of 131.5° C, was placed in a dewar tube equipped with a 5-junction thermocouple and a mechanical stirrer, and cooled with liquid air. The mass became more and more viscous until a gradual solidification to a clear glass took place not far above liquid-air temperatures. Such a condition precluded the possibility of the isolation of any component by simple equilibrium melting of the undiluted oil.

To investigate the feasibility of crystallization from a solvent, an exploratory experiment in the small glass apparatus of Leslie [10] was then made on a distilled fraction boiling at 131.85° C. To a volume of the oil, an equal volume of liquid propane was added and the mixture stirred and cooled. This was added dropwise to 2 volumes of liquid methane. The crystals which developed, though of a pasty texture, were separated and freed of propane. The following results were obtained:

Refractive index of crystal fraction	1.4286
Refractive index of mother liquor	1.4283
Refractive index of original	1.4284

Since these results were not very satisfactory, the effect of increasing the relative amount of propane was observed on the same material, using 3 volumes of propane. The crystals were still rather gummy, but more encouraging results were obtained, the refractive index of the crystal fraction being 1.4293 and that of the mother liquor, 1.4275. This difference in refractive indices, though small, indicated that separation by this method was possible. A similar trial using 2 volumes of propane to 1 volume of oil gave essentially the same results as the second experiment.

3. CRYSTALLIZATION OF THE DISTILLATION FRACTIONS

Since crystallization in the manner outlined above was the only method which gave promise of eventual separation of the pure component, all fractions amenable to this treatment (the 1,800 ml of material previously noted) were crystallized in the large metal centrifuge as described by Leslie.[10] Typical data are given in table 1.

The technic of these crystallizations requires experience and judgment and no set rules can be given for all fractions. The proportions of solvent and solute were varied according to the judgment of the operator; most frequently, 2 volumes of propane, 1 volume of oil, and 2 volumes of methane were used.

The fractions having a refractive index below 1.4260 gave poor results generally, and few attempts were made to crystallize them. Possibly significant is the fact that better separation, as judged by refractive index, occurred with cuts having boiling points above 131.7°. This might be interpreted as evidence for a second naph-

[10] R. T. Leslie, BS J. Research **10**, 609-618 (1933) RP552.

thene boiling at a lower temperature than the one isolated. If this were true, the mother liquors of the lower-boiling fractions would consist principally of a eutectic of the two naphthenes, whereas the higher-boiling cuts would contain mainly paraffinic material as an impurity.

TABLE 1.—*Typical results of crystallization from liquid propane and methane* [1]

Original fraction		Crystal fraction		Mother liquor	
Boiling range	n_D^{25}	Volume	n_D^{25}	Volume	n_D^{25}
°C		ml		ml	
131.8 — .8₅	1.4287	34	1.4289	17	1.4248
131.7₅ — .8	1.4282	29	1.4289	29	1.4263
131.6 — .7₅	1.4282	19	1.4287	30	1.4270
131.7 — .9	1.4284	49	1.4294	39	1.4266
132.0 —	1.4277	40	1.4291	23	1.4247
132.0 — .8₅	1.4277	35	1.4290	18	1.4236
131.3 — .5₅	1.4263	47	1.4265	8	1.4245
131.4 — .5	1.4276	75	1.4279	7	1.4251
132.5	1.4249	6	1.4252	42	1.4246
131.9 — 132.5	1.4266	30	1.4280	22	1.4235

[1] These fractions had not been treated with silica gel and the refractive indices are too high by about 0.001.

4. FURTHER SEPARATION OF THE COMPONENT

At this juncture several new developments were utilized. First, selective adsorption by silica gel was used to remove the confusing and troublesome residual amounts of aromatic compounds. Second, fractions only moderately concentrated in the naphthene were distilled with glacial acetic acid to yield more fractions susceptible of crystallization. Third, a still of small capacity made further distillation of certain fractions feasible.

With the apparatus and technic described by Mair and White,[11] the separation with silica gel was continued until all the material was freed of aromatic compounds. In the case of the distillates, the change in refractive index resulting from this treatment varied quite widely, being usually about 0.0010 to 0.0015, but in some cases, notably distillation residues, differences as great as 0.0045 were attained. The refractive indices of the crystal fractions thus far obtained were lowered about the same amount as were those of the mother liquors; i. e., 0.0010 to 0.0015, which indicated that the aromatic hydrocarbons had not been completely removed by crystallization.

After this treatment, the fractions of the distillate that did not crystallize were distilled in a 30-plate fractionating column with glacial acetic acid.[12] By this means, an additional concentration of naphthenes was effected, proper cuts being combined as far as possible.

In order to concentrate a suspected second naphthene into cuts somewhat removed from those containing the bulk of the main component, the fractions resulting from the acetic acid process were systematically distilled in a spiral column coated with carborundum and equipped with a vacuum jacket and reflux regulator. In the course of this distillation, the mother liquors from the crystallization

[11] B. J. Mair and J. D. White, J. Research NBS **15**, 51 (1935) RP809.

[12] The process of distillation with glacial acetic acid will be described in a forthcoming paper by S. T. Schicktanz. It operates through the formation of minimum azeotropic mixtures and gives a separation of material in certain cases which would fractionate very slowly when distilled as undiluted oil.

from liquid methane were combined with the major portion of the distillate, as were certain fractions resulting from the systematic distillation of lower boiling fractions, as well as the nonaromatic portion of (1) the oil adsorbed by silica gel and (2) some residues from the isolation of ethylbenzene.

Various portions of oil accumulating as a result of this technic were crystallized from methane with the following results: (1) fractions having a refractive index below 1.425 showed no separation on crystallization; (2) fractions having a refractive index above 1.425, but boiling at a temperature lower than 131.5° C, gave little apparent separation as judged by refractive index; (3) crystallization of a cut with boiling range 130.9 to 131.0° C, $n_D^{25}=1.4255$, gave little separation, but the crystal fraction in this case boiled at a lower temperature than the mother liquor; (4) the boiling points of all other crystal fractions rose with increasing purity (see table 2); (5) the mother liquors on redistillation boiled for the most part at temperatures below 131.5° C.

After removing the main component as far as possible by crystallization from all material available, the crystal fractions were in turn systematically recrystallized. The progress of this systematic separation can best be judged by the constants of typical fractions in table 2. As a result, a portion was isolated which by a final crystallization gave these fractions after removal of propane:

Crystal fraction, 100 ml, $n_D^{25}=1.4297$, fp$=-112.9_0$;

Mother liquor, 40 ml, $n_D^{25}=1.4295$, fp$=-114.4_0$.

Because of the similarlity in properties of the mother liquor and the crystal fraction, further purification was deemed impracticable. This crystal fraction is designated in the following section as the "best sample" from petroleum.

TABLE 2.—*Data illustrating the rise in boiling point of the crystal fraction with increasing purity* [1]

Mother liquor	Crystal fractions		
n_D^{25}	Boiling point	Freezing point	n_D^{25}
	°C	°C	
1.4285	131.5	−112.9	1.4298
1.4280	131.4	−115.7	1.4295
1.4222	----------	−116.7	1.4292
1.4230	----------	−118.0	1.4283
1.4240	130.6	−125.5	1.4280
1.4230	130.9	−125.0	1.4276
----------	131.1	----------	1.4278
----------	130.9	----------	1.4268

[1] The constants in this table are not highly accurate and are to be considered only comparative. The freezing points were determined with a 5-junction thermocouple in a dewar tube, the boiling points in a Cottrell boiler.

III. PROPERTIES AND IDENTIFICATION OF THE ISOLATED ETHYLCYCLOHEXANE

1. PREPARATION AND PURIFICATION OF THE SYNTHETIC HYDROCARBON

The physical properties of the crystal fraction obtained above pointed to its identity as ethylcyclohexane, but because of discrepancies in the values for the physical constants of ethylcyclohexane reported in the literature, it was first necessary to synthesize the hydrocarbon in order to compare its properties with those of the material isolated from petroleum.

A 750-ml lot of ethylbenzene[13] was distilled in a locket-chain column, and a number of fractions, having identical boiling points, and refractive indices were obtained. Freezing curves of the various fractions were taken to establish their purity. The freezing points varied about 0.6° C, the highest being identical with that of the very pure sample of J. Timmermans [14] previously tested by the authors. This sample of ethylbenzene was then hydrogenated over a nickelized alumina catalyst after the manner of Zelinsky.[15]

The hydrogenated material (350 ml) was filtered through silica gel to remove the remaining ethylbenzene. As the boiling point of the purified naphthene was thought to be too low, ca. 129.5° C, it was crystallized once from difluorodichloromethane. (The undiluted liquid partially crystallized on cooling but the mixture was too viscous to be separable.) The crystal fraction now had a boiling point of 130.5° C and an initial observed freezing point of −113.1° C.[16]

Since it has been reported [17] that methylcyclohexane is formed during the hydrogenation of ethylbenzene, the mother liquor (90 ml) was distilled in a small still. The combined initial fractions had a low refractive index and a boiling point of 126.8° C. The refractive index of the residue rose slightly (0.0002), indicating a trace of residual aromatics. The large middle portion had a boiling point of 131.8$_5$° C, as determined in a Cottrell apparatus, and on freezing exhibited the behavior of a very pure substance. It is designated in table 3 as "synthetic." Its freezing curve [18] is shown in figure 2. The crystal fraction was similarly distilled until 25 percent was taken off. This portion had a low boiling point. The remaining 75 percent, though not as pure as the distilled mother liquor, showed a higher freezing point, −111.5$_9$° C, than before distillation.

2. PROPERTIES OF THE MATERIAL ISOLATED FROM PETROLEUM

As pointed out in the previous section, the virtual limit of separation by crystallization had been reached for the "best sample" from petroleum. Owing to the difficulties attendant upon the additional preparation of concentrates of material to such a degree of purity,[19]

[13] This was obtained through the courtesy of the George Washington University. It was synthesized by students using the Friedel-Crafts method.
[14] J. Timmermans and F. Martin, J. chim. phys. **23**, 758–759 (1926).
[15] N. Zelinsky and W. Kommarewsky, Ber. deut. chem. Ges. **57**, 667 (1924).
[16] Measured with a platinum resistance thermometer. See B.J. Mair, BS J. Research **9**, 457 (1932) RP482.
[17] F. Sabatier and J. B. Senderens, Compt. rend. **132**, 1254 (1901).
[18] Crystallization was induced by seed crystals produced outside in a small dewar tube and added when the temperature was slightly below the freezing point.
[19] It should be noted that the sample under consideration constituted the bulk of the purified material. There were, of course, small amounts of mother liquors.

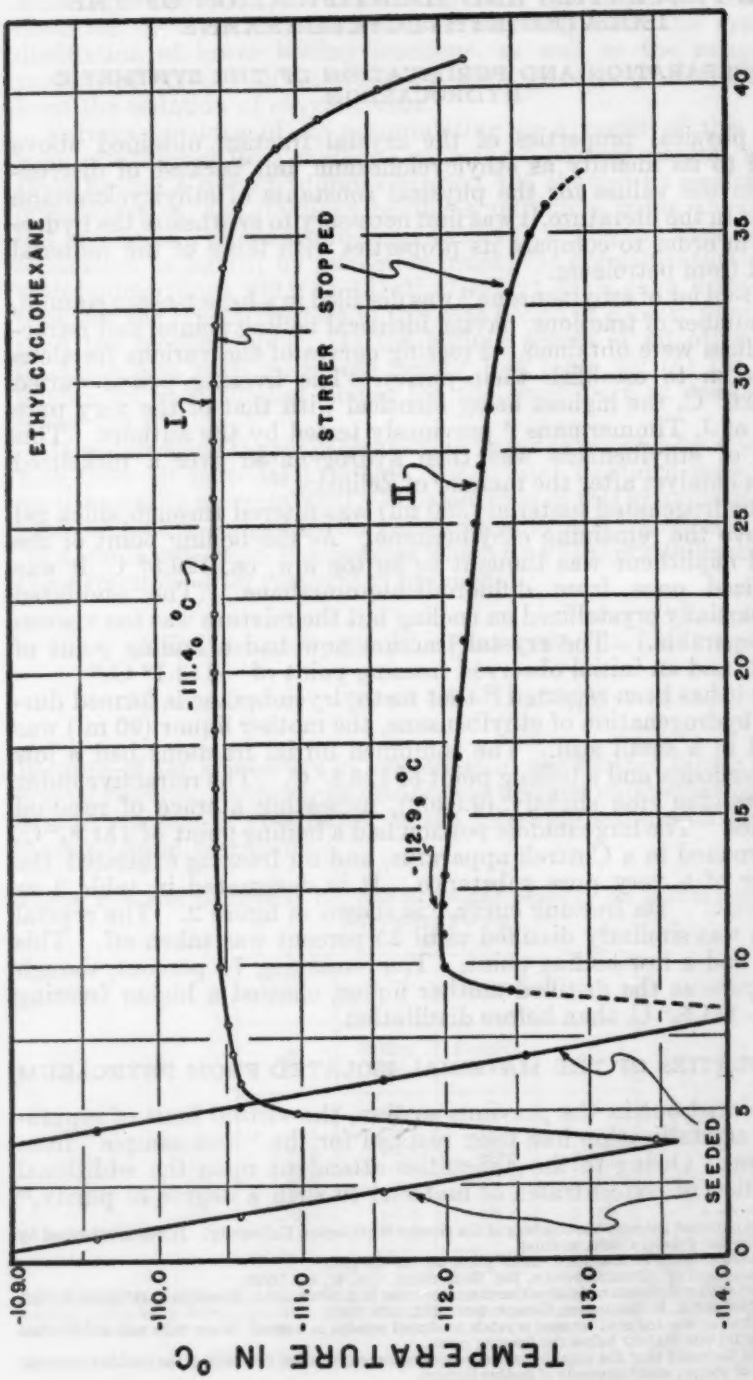

FIGURE 2.—*Time-temperature cooling curves of synthetic sample, I, and petroleum fraction, II.*

it was decided to examine this material to see if it was a nearly pure substance.

The empirical formula of the hydrocarbon was established by determining the carbon-hydrogen ratio. As a result of two combustion experiments, the mean ratio, moles H_2O/moles CO_2, was found to be 1.0033 ± 0.0006. This agrees well with the value for a pure naphthene, C_nH_{2n}, and indicates about 3-mole percent of impurity if an isononane is the contaminant.

The molecular weight of the isolated material was found to be the same as that of the synthetic ethylcyclohexane by direct comparison of the freezing point lowerings of the two samples in nitrobenzene. This showed the isolated product to be an octonaphthene.

The boiling range of the petroleum sample was determined in the apparatus of Mair.[20] In distilling 50 ml of a 65-ml sample at the rate of 1 ml per minute, the temperature rose 0.22° C.

The freezing-point curve is shown in figure 2. The material had a freezing range of 0.5° C, which indicated that it was approximately pure. This was confirmed by microscopical observation of the liquid during crystallization.[21] A drop of the material between 2 microscope coverglasses was placed in the dewar flask, which contained no liquid and was maintained at a temperature slightly below the freezing point. Crystallization was induced by seeding. Owing to the viscosity of the liquid, the crystals grew exceedingly slowly under these conditions and were closely packed together. Crystals suitable for examination were obtained only after partial melting and recrystallization. They were then distinctive in habit, having well defined interfacial angles and an extinction nearly parallel to the long edges. All crystallization occurred within a very narrow temperature interval. Only a few degrees below the freezing point, shrinkage cracks developed in the crystals to an extent that would not have been possible had there been any appreciable amount of residual mother liquor. Although the temperature was carried 25° C below the freezing point, no new crystalline phase appeared. A similar examination of the synthetic ethylcyclohexane was made. The entire behavior and form of its crystals were indistinguishable from those of the material isolated from petroleum.

A comparison of the physical properties of the synthetic and the petroleum samples with some values reported in the literature [22] may be made by referring to table 3.

[20] See footnote 16.

[21] This examination was made by Charles Proffer Saylor, of this Bureau, in the apparatus described by him. W. H. Smith, C. P. Saylor, and H. J. Wing. BS J. Research **10**, 484 (1933) RP544.

[22] Ethylcyclohexane has been synthesized many times with varying results as to the physical properties. For earlier preparations consult Beilstein's Handbuch der organischen Chemie. Other recent preparations are by F. K. Signaigo and P. L. Cramer, J. Am. Chem. Soc. **55**, 3331 (1933); and R. Adams and J. R. Marshall, J. Am. Chem. Soc. **50**, 1970 (1928).

FIGURE 2.—*Time-temperature cooling curves of synthetic sample, I, and petroleum fraction, II.*

TABLE 3.—*Comparison of the physical constants of ethylcyclohexane from petroleum with various synthetic preparations*

Source	d_4^{20}	n_D^{20}	cst in aniline	Boiling point 760 mm	Freezing point
	g/ml		°C	°C	°C
From petroleum ("best sample")	[e] 0.78573	[d] 1.42980	44.5	[g] 131.5	[h i] −113.0
Synthetic:					
Rose and White	[e] .78804	[d] 1.43079		[g] 131.8	[h] −111.4
Timmermans [a]				131.8	−128.9
Garner and Evans [b]	.7825	[e] 1.4297	[f] 43.8	131.6	

[a] Bul. Soc. Chim. Belg. 36, 503 (1927).
[b] J. Inst. Petroleum Tech. 18, 751–778 (1932).
[c] ±0.00002. Determined by the Division of Weights and Measures of this Bureau.
[d] ±0.00005. Determined on a calibrated Abbe refractometer (Valentine design).
[e] Calculated from value at 20° C, using $dn/dt = 0.00045$ per °C.
[f] Aniline point.
[g] ±0.05. Determined in a Cottrell boiling-point apparatus.
[h] ±0.05° C. Determined with a platinum-resistance thermometer.
[i] Initial observed freezing point.

All the boiling points are in good agreement. The difference between the boiling points of the isolated and synthetic hydrocarbons, 0.28° C, is not large, considering the boiling range of the former.

The difference in the refractive indices, 0.0010, leads to a similar conclusion, with regard to impurities, as that drawn from the combustion analysis and shows about the same paraffin content.

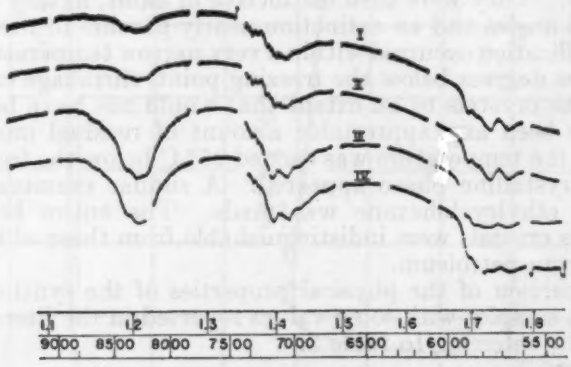

FIGURE 3.—*Infrared absorption curves.*

Records of the transmission in the near infrared through 10-cm cell lengths of solutions of the synthetic sample and petroleum fraction of ethylcyclohexane. The solvent was purified carbon tetrachloride and the concentrations were for the synthetic sample, curves II, III, 0.0570 and 0.2974 molal, respectively, and for the petroleum fraction, curves I, IV, 0.0595 and 0.2854 molal, respectively.

In order to give definite proof of the identity of the isolated hydrocarbon, the freezing point of a mixture of 20 ml of the synthetic material and 10 ml of the mother liquor from the final crystallization of the "best sample" was taken. The mother liquor froze 1.3° C below the synthetic, and the mixture 0.4° C below. Excluding the possibility of two hydrocarbons having nearly the same freezing point and forming a continuous series of solid solutions (a condition found at present only in stereoisomers) this proves the compounds to be identical.

The infrared absorption spectra of the petroleum and synthetic samples have been recorded by the courtesy of O. R. Wulf and U. Liddel, of the U. S. Bureau of Chemistry and Soils. Both spectra (figure 3) have the characteristics of a substituted cyclohexane,[23] and their similarity is additional evidence for the identity of the petroleum sample.

The freezing point of the ethylcyclohexane from petroleum is lower than that of the synthetic material by 1.5° C. An experimental determination of the cryoscopic constant ($K=\Delta t/x_1$, where x_1 is the mole fraction of the solute) by adding pure *n*-nonane to the ethylcyclohexane gave a value of 31° C/mole percent. If this value is used, the purity of the "best sample" from petroleum is calculated to be about 95 mole percent.

Because of the fact that the fractions containing the bulk of the ethylcyclohexane were not crystallizable, it was not possible to determine the purity of those fractions and, hence, the amount of ethylcyclohexane from their freezing points (thermal analysis). Moreover, the probable presence of a second naphthene makes an estimation of the content by means of refractive index untrustworthy. Therefore, until work on this second component is completed, one can only say that the total content (judged by refractive index) of ethylcyclohexane in this petroleum does not exceed 0.1 percent.

The authors are deeply appreciative of the technical guidance of the late Dr. E. W. Washburn at the inception of this work.

WASHINGTON, April 15, 1935.

[23] U. Liddel and C. Kaspar, BS J. Research 11, 599 (1933) RP610.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP818

Part of Journal of Research of the National Bureau of Standards, Volume 15, August 1935

EFFECT OF PROTECTIVE COATINGS ON THE ABSORPTION OF MOISTURE BY GELATIN-LATEX GAS-CELL FABRICS

By David F. Houston

Abstract

The effects of six variations in protective coating on the percentage of moisture held at 21° C (70° F) and various relative humidities, and the rates at which this moisture is absorbed, have been determined by a static method for two lightweight gelatin-latex gas-cell fabrics. The two fabrics differed only in their content of gelatin (which was plasticized with polyglycerol). At relative humidities below 94 percent the amount and distribution of paraffin do not affect the final amounts of moisture held by the fabrics. Slightly higher values are found for varnish coatings, as compared with paraffin coatings, because of the hygroscopicity of the varnishes. At relative humidities above 94 percent, mold growth and leaching of gelatin and polyglycerol by moisture cause the fabrics to lose weight before the maximum possible absorption of moisture can occur. Increasing the thickness of the paraffin lowers the rate of absorption of moisture. Application to both surfaces of the fabric reduces the rate much more than a comparable increase in weight of paraffin on one side only. When varnish containing aluminum powder is used, an increased rate is found. Reduction of the amount of the gelatin layer gives a reduction in the total amount of moisture held, and gives smaller differences for variations in protective coatings. A consideration of the absorptive properties of the fabric constituents, based on available data, and of the permeabilities of the materials surrounding the very hygroscopic gelatin layer, indicates that the combination of these factors readily explains the moisture absorption relations of the completed fabrics.

CONTENTS

	Page
I. Introduction	163
II. Materials	164
III. Apparatus and procedure	164
IV. Experimental results	165
V. Discussion of results	168
VI. Conclusions	172

I. INTRODUCTION

In the manufacture of gas-cells from gelatin-latex fabric, it is customary to coat one or both surfaces of the cell with paraffin as a protection against the absorption of moisture or the loss of some constituent of the fabric. It was shown in a previous article on this subject [1] that the rate of absorption of moisture by this type of fabric is retarded by the application of paraffin, though the total absorption remains practically unchanged. The Goodyear Zeppelin Corporation kindly submitted for our study samples of the standard lightweight

[1] G. M. Kline, J. Research NBS 14, 67 (1935) RP758. This article contains references to the previous investigations of these materials.

fabric, and of an experimental fabric containing less gelatin, which were coated by them with different amounts of paraffin or other type of protective coating. This investigation was made to determine the effects of variations in amount, distribution, and type of protective coating on the rate and amount of absorption of moisture by these fabrics. The results obtained are considered on the basis of the present study coupled with pertinent information obtained from other sources.

II. MATERIALS

The fabrics studied are listed and described in table 1; the fabric designated as Q39–A–10 contains less gelatin than the standard lightweight fabric Q39–A–2, and is hereafter referred to as "improved fabric." The amount of paraffin on the samples was determined at the beginning of the investigation. Samples 1 to 6 are referred to as set 1, and samples 7 to 12 as set 2.

TABLE 1.—*Description of materials*

Sample	Fabric	Type of coating	Weight of coated fabric	Amount of coating indicated by manufacturer		Total paraffin found
				Inside	Outside	
			oz/yd²	oz/yd²	oz/yd²	oz/yd²
1	Goodyear Code Q39–A–2.	Paraffin	5.41	----	0.2	0.3
2	do	do	5.66	----	.4	.6
3	do	do	5.83	0.2	.2	.7
4	do	do	5.96	.2	.4	.8
5	do	Paraffin and Goodyear Code 755C aluminum paint.[1]	5.94	.2	{.2 paraffin .2 Al paint}	[3].6
6	do	Aluminum powder in flexible spar varnish.[2]	7.30	----	----	----
7	Goodyear Code Q39–A–10.	Paraffin	5.58	----	.2	.35
8	do	do	5.82	----	.4	.6
9	do	do	6.00	.2	.2	.8
10	do	do	5.96	.2	.4	.8
11	do	Paraffin and Goodyear Code 755C aluminum paint.[1]	6.07	.2	{.2 paraffin .2 Al paint}	[3].7
12	do	Aluminum powder in flexible spar varnish.[2]	6.95	----	----	----

[1] The aluminum paint and the flexible spar varnish are apparently of different composition.
[2] Flexible spar varnish containing aluminum dust is applied to both surfaces. Total weight of coating for sample 6 is 2.2 oz/sq yd; for sample 12 is 1.8 oz/sq yd.
[3] Value may be slightly high as a result of breakdown of the paint coating.

III. APPARATUS AND PROCEDURE

The determination of the amounts of moisture held by the fabrics was made by the static method described by Evans and Critchfield,[2] and used in the previous paper [3] on this subject. In this method a sample, measuring 2 by 8 inches, was suspended on a wire passing through a glass tube of small bore in the stopper of a 6-ounce bottle. The glass tube was closed between weighings by a paraffined cork through which the wire passed. The sample was weighed without removal from the bottle by placing the latter on a bridge over the balance pan and suspending the wire from the balance hook. The

[2] W. D. Evans and C. L. Critchfield, BS J. Research **11**, 151 (1933) RP583.
[3] See page 68 of reference 1.

following reagents, used to maintain the various humidities,[4] were placed in the bottom of the bottles.

Relative humidity (percent)	Reagent
0	Phosphorus pentoxide.
86	Saturated solution of potassium chloride.
94	Saturated solution of potassium nitrate.
97	Saturated solution of potassium sulphate.
100	Water.

All the samples were conditioned at 65 percent relative humidity and 21° C (70° F), the standard atmosphere, until constant weight was obtained. The edges were then sealed with paraffin by dipping them into a solution of Parowax in petroleum ether. The samples were again conditioned to the standard atmosphere, and the added weight of paraffin was determined, before exposure to the various humidities was begun. Weighings were made at suitable intervals until no sample, after a week's time, showed an increase greater than 0.3 percent by weight, calculated on the uncoated fabric. The tests were all made in a room held at a temperature of $21 \pm 1°$ C. The controls of temperature and humidity were shut off several times during the latter part of the investigation for periods approximating 1½ days each; these periods are reflected in the results by slight but unimportant irregularities.

IV. EXPERIMENTAL RESULTS

The data obtained for the absorption of moisture by the fabrics described above are presented in tables 2 to 6. For intercomparison, the results are all calculated as percentage change in weight based on the weight of the uncoated fabric.

TABLE 2.—*Percentage change in weight of light-weight gelatin-latex gas-cell fabrics, which had been conditioned in air at 21° C and 65 percent relative humidity, when exposed at 0 percent relative humidity*

Time in days	Percentage change in weight of samples—											
	1	2	3	4	5	6	7	8	9	10	11	12
¼	−1.2	−0.9	−0.4	−0.2	−0.4	−0.9	−1.7	−1.1	−0.2	−0.3	−0.2	−0.5
½	−2.8	−2.4	−1.0	−0.7	−1.7	−2.1	−2.8	−2.6	−0.7	−0.6	−0.7	−1.4
1	−4.3	−3.7	−1.7	−1.2	−2.0	−3.5	−4.0	−3.8	−1.2	−1.2	−1.3	−2.4
1	−6.7	−6.2	−4.4	−3.3	−4.9	−7.0	−5.7	−5.8	−3.3	−3.3	−3.5	−5.2
2	−7.2	−7.0	−5.9	−4.9	−6.6	−8.1	−6.2	−6.5	−4.8	−4.8	−5.0	−6.3
3	−7.4	−7.3	−6.5	−5.3	−7.3	−8.5	−6.5	−6.8	−5.6	−5.6	−5.7	−6.7
4											−6.1	−6.9
5	−7.6	−7.5	−7.0	−6.7	−8.0	−8.9	−6.7	−7.1	−6.3	−5.9		
7	−7.7	−7.6	−7.2	−7.1	−8.3	−9.0	−6.8	−7.3	−6.6	−6.7	−6.7	−7.2
14	−7.8	−7.7	−7.6	−7.5	−8.6	−9.2	−7.0	−7.5	−7.0	−7.2	−6.9	−7.3
21	−7.7	−7.7	−7.7	−7.6	−8.8	−9.3	−7.0	−7.6	−7.1	−7.3		
25											−7.1	−7.4
28	−7.8	−7.7	−7.7	−7.6	−8.8	−9.3	−7.0					
32								−7.7	−7.2	−7.4		
35	−7.8	−7.7	−7.7	−7.6							−7.1	−7.4
36								−7.7	−7.3	−7.4		
39					−8.8	−9.4	−7.1					

[4] Int. Crit. Tables 1, 67; (McGraw-Hill Book Co., New York, 1926).

TABLE 3.—*Percentage change in weight of light-weight gelatin-latex gas-cell fabrics, which had been conditioned in air at 21° C and 65 percent relative humidity, when exposed at 86 percent relative humidity*

Time in days	Percentage change in weight of samples—											
	1	2	3	4	5	6	7	8	9	10	11	12
¼	0.5	0.4	0.2	0.1	0.5	0.3	0.4	0.4	0.1	0.1	0.1	0.2
½	1.3	1.0	0.5	0.3	0.9	0.7	1.2	0.9	0.3	0.3	0.3	0.5
¾	2.1	1.8	0.9	0.6	1.4	1.3	2.0	1.7	0.5	0.5	0.5	0.8
1	5.8	5.1	2.7	1.8	3.6	3.8	4.6	4.2	1.7	1.7	1.7	2.8
2	7.9	7.3	4.4	3.0	5.7	5.9	6.2	5.8	2.9	2.9	2.9	4.4
3	9.4	8.7	5.7	4.0	7.1	7.3	7.0	6.7	3.8	3.7	3.8	5.4
4											4.5	6.1
5	10.6	10.3	7.5	5.5	9.2	9.3	7.8	7.7	5.2	5.1		
7	11.0	10.7	8.6	6.5	10.4	10.5	8.2	8.1	6.0	5.9	5.8	7.2
14	11.6	11.8	10.4	8.8	12.3	12.3	8.5	8.6	7.5	7.5	7.3	8.0
21	11.8	12.0	11.2	10.0	12.8	12.7	8.4	8.7	8.1	8.1		
25											7.7	7.7
28	11.7	12.0	11.3	10.6	13.0	12.9	8.4					
29											7.9	7.9
35	11.9	12.1	11.5	11.0							7.9	7.9
42			11.6	11.2				8.4	8.5	8.5	8.0	7.9
43					13.0	12.9	8.3					
56				11.4	13.3		8.1	8.5	8.5	8.5	8.1	
63							8.1	8.6	8.7	8.6	8.1	

TABLE 4.—*Percentage change in weight of light-weight gelatin-latex gas-cell fabrics, which had been conditioned in air at 21° C and 65 percent relative humidity, when exposed at 94 percent relative humidity*

Time in days	Percentage change in weight of samples—											
	1	2	3	4	5	6	7	8	9	10	11	12
¼	0.6	0.5	0.2	0.2	0.7	0.4	0.6	0.5	0.2	0.2	0.2	0.3
½	1.7	1.6	0.6	0.5	1.3	1.1	1.7	1.4	0.5	0.4	0.5	0.7
¾	3.0	2.7	1.2	0.9	2.2	1.9	2.9	2.4	0.9	0.8	0.9	1.4
1	8.2	7.7	3.9	3.2	6.2	5.8	7.1	6.6	2.8	2.8	2.9	4.4
2	12.3	11.6	6.4	5.4	10.0	9.4	10.3	10.0	4.8	4.8	5.0	7.1
3	15.3	14.5	8.5	7.3	12.9	12.0	12.6	12.3	6.4	6.4	6.6	9.2
4											8.0	10.9
5	19.3	18.6	11.6	10.1	17.3	16.2	15.6	15.5	9.0	9.1		
7	22.0	21.4	14.2	12.3	20.4	19.2	17.6	17.4	10.8	11.5	10.9	14.1
14	27.1	26.8	19.7	17.5	26.8	25.3	21.0	20.6	15.2	15.6	15.1	18.3
21	29.6	29.5	23.3	21.1	29.6	28.5	22.1	22.3	17.9	18.4		
25											18.2	20.3
28	29.5	30.5	25.5	23.7	31.5	30.7	22.9					
29											19.0	21.1
32								22.3	19.9	20.6		
35	28.1	30.9	26.9	25.4							19.9	21.6
39					32.0	30.9	22.5					
42			27.6	26.8				23.0	21.5	22.7	20.6	21.8
43					32.4	30.4	22.9					
49			27.2	27.6	32.4		23.0	23.3	22.2	22.0	21.1	21.5
56				27.6	32.2		22.8	23.3	22.5	23.3	21.8	
63							22.3	23.6	22.9	23.9	22.1	
74								22.5			22.7	

TABLE 5.—*Percentage change in weight of light-weight gelatin-latex gas-cell fabrics, which had been conditioned in air at 21° C and 65 percent relative humidity, when exposed at 97 percent relative humidity*

Time in days	Percentage change in weight of samples—											
	1	2	3	4	5	6	7	8	9	10	11	12
½4	1.0	0.7	0.3	0.2	0.5	0.5	0.7	0.7	0.3	0.3	0.2	0.3
⅛	2.4	1.9	0.8	0.6	1.2	1.3	2.0	1.7	0.7	0.6	0.5	0.9
¼	4.2	3.3	1.5	1.1	2.3	2.3	3.5	3.0	1.2	1.1	1.1	1.7
1	11.1	9.1	4.8	3.4	7.3	6.9	8.8	8.1	3.9	3.6	3.3	5.3
2	16.9	14.1	8.2	5.9	12.3	11.5	13.5	12.3	6.8	6.3	5.8	8.9
3	21.5	18.2	11.1	8.2	16.2	15.1	17.0	15.5	9.1	8.5	7.8	11.7
4											9.8	14.2
5	28.3	24.5	15.8	11.9	23.5	21.4	22.5	20.7	13.0	12.4		
7	34.2	30.2	20.0	15.2	29.2	26.5	26.6	24.4	16.0	15.4	14.2	19.7
14	48.0	43.1	29.9	25.6	43.2	39.4	36.9	33.8	24.5	23.7	24.5	29.5
21	55.9	51.0	37.5	34.7	52.7	49.1	43.4	40.6	31.4	30.1		
25											31.4	38.3
28	50.1	57.0	45.4	42.6	60.6	56.7	48.7					
29											34.4	41.4
32								48.3	39.7	38.9		
35	40.5	51.6	51.8	45.5							38.0	42.5
39					66.3	53.4	53.6					
42			56.8	48.2				52.2	45.4	46.1	41.6	44.2
49			52.1	52.1	69.9		55.7	53.0	47.5	48.9	44.4	42.9
56				49.7	67.2		54.8	52.9	46.8	50.1	46.4	
63							53.0	54.0	47.7	50.8	48.0	
70								54.6	47.3	48.0		
74								54.5			48.8	

TABLE 6.—*Percentage change in weight of light-weight gelatin-latex gas-cell fabrics, which had been conditioned in air at 21° C and 65 percent relative humidity, when exposed at 100 percent relative humidity*

Time in days	Percentage change in weight of samples—											
	1	2	3	4	5	6	7	8	9	10	11	12
½4	1.2	0.9	0.4	0.3	0.9	0.7	0.9	0.8	0.4	0.4	0.3	0.4
⅛	3.0	2.3	1.3	0.7	2.3	1.8	2.4	2.0	1.0	1.0	0.8	1.0
¼	5.1	4.0	1.9	1.3	4.1	3.1	4.0	3.5	1.8	1.8	1.4	1.8
1	13.2	10.6	6.0	4.3	12.5	9.3	10.1	9.2	5.7	5.5	4.5	5.7
2	19.5	16.7	10.3	7.5	21.9	15.6	15.8	14.6	10.2	9.4	7.9	9.6
3	24.8	22.0	14.0	10.5	29.3	20.5	19.8	18.6	13.8	12.1	10.7	12.6
4											13.3	15.3
5	33.1	30.4	20.8	15.4	41.6	28.5	26.6	25.1	20.2	17.1		
7	40.9	38.4	27.1	19.8	49.6	35.0	32.5	30.4	25.3	21.4	19.9	21.8
14	63.3	59.3	43.5	33.5	72.2	52.4	48.2	45.6	41.0	34.9	33.1	35.4
21	79.0	77.5	59.6	46.6	90.6	67.8	61.5	58.2	54.2	46.4		
25											56.1	52.6
28	65.0	77.3	73.9	58.4	107.1	82.8	69.7					
29											58.1	52.6
32								73.8	73.0	60.2		
35	48.1	62.3	82.7	67.7							68.0	53.9
39					120.2	63.7	82.5					
42			75.3	72.5				87.4	75.1	67.2	70.3	54.8
49			67.6	69.6	135.9		95.1	90.2	80.6	66.1	74.0	52.4
56				60.4	130.7		100.6	94.7	78.8	66.3	74.4	
63							100.2	90.6	77.4	66.9	74.5	
67											78.5	

The maximum values for gain in weight of the materials, calculated to percentage gain based on the weight of the uncoated fabric at 0 percent relative humidity, are collected in table 7. This table also indicates the time required for the attainment of these values, and the approximate periods of time after which mold growth became apparent on visual inspection. This mold growth appeared after various periods of time upon practically all the samples exposed at 21° C to relative humidities of 94 percent or over.

TABLE 7.—*Maximum moisture contents of light-weight gelatin-latex gas-cell fabrics observed at various relative humidities (based on weight of dry, uncoated fabric), and times elapsed before mold growth became visible*

Sample	Values at various relative humidities of—											
	65%	80%			94%			97%			100%		
	Moisture content	Moisture content	Period of exposure preceding—		Moisture content	Period of exposure preceding—		Moisture content	Period of exposure preceding—		Moisture content	Period of exposure preceding—	
			Maximum gain	Visible mold growth		Maximum gain	Visible mold growth		Maximum gain	Visible mold growth		Maximum gain	Visible mold growth
	%	%	*Days*	*Days*	%	*Days*	*Days*	%	*Days*	*Days*	%	*Days*	*Days*
0 [a]	8.5	21.3	21	------	41.2	21	ca10	85.4	42	ca10	115.3	35	ca10
1	8.5	21.4	35	------	40.6	21	24	69.1	21	14	94.2	21	14
2	8.3	21.5	35	------	41.8	35	------	70.1	28	21	92.3	21	21
3	8.3	20.9	42	------	38.2	42	------	69.9	42	28	97.9	35	28
4	8.2	20.6	56	------	38.1	49	------	64.6	49	28	86.7	42	28
5	9.7	24.2	56	------	45.2	43	35	86.3	49	28	158.7	49	21
6	10.4	24.7	43	------	44.5	39	28	73.0	28	21	101.8	28	21
7	7.6	16.8	14	------	32.4	49	39	68.7	49	39	115.9	56	39
8	8.3	17.8	21	------	33.9	63	32	67.5	70	32	111.0	56	32
9	7.9	17.3	63	------	32.6	63	32	59.3	63	32	94.8	49	21
10	8.0	17.3	63	------	33.8	63	42	62.9	63	32	80.6	42	21
11	7.6	16.4	56	------	32.1	74	------	60.2	74	25	92.1	67	25
12	8.0	16.5	29	------	31.2	42	29	54.4	42	25	64.6	42	25

[a] Values for sample 0 are calculated from an experiment by G. M. Kline on uncoated edge-sealed Q39-A-2 fabric (J. Research NBS 14, 80 (1935) table 13) RP758. Other numbers refer to samples described in table 1.

Differences in the rates of attainment of the maximum values are apparent in the results for various samples in a set. These differences become increasingly characteristic with increasing relative humidity up to 97 percent. At a relative humidity of 100 percent, irregularities become great enough to interfere with comparisons. Accordingly, the rates of approach to maximum values at 97 percent relative humidity are plotted in figure 1 for comparison. These rates are based on percentages of total gains in weight of fabrics conditioned at 65 percent relative humidity and 21° C.

In connection with the results shown in figure 1, it should be remembered that the weights of the protective coatings on samples 6 and 12 are 2.2 and 1.8 oz/sq yd, respectively, whereas those on the other samples are less than 0.9 oz/sq yd. On an airship of the GZ–1 type, such as the *Macon*, 54,000 sq yd of fabric are required for the gas cells. If the heavier protective coatings were to be used on the cells in place of the lighter ones, there would be a minimum difference in weight of approximately 1.5, tons aside from any considerations of absorption of moisture.

V. DISCUSSION

In order to discuss adequately the effects of variations in protective coatings on gelatin-latex fabrics, it is appropriate to determine what the operative factors are in the problem. These resolve themselves essentially into factors causing gains in weight on exposure to humid atmospheres and those causing losses under the same conditions. The factors causing gains in weight may further be viewed with respect to amount and rate—the properties of absorptivity and permeability.

The nature and relative location of the materials in the gelatin-latex gas-cell fabrics investigated are indicated in figure 2. The protective coating may or may not be present on the inner surface of the fabric. In all cases here considered, the edges are sealed with paraffin as described in section III, and indicated in figure 2.

Information on the absorptive properties of most of the materials used is available in the literature. Pertinent values have been collected and are presented in table 8. For an uncoated fabric it may be seen that the chief absorbing materials are cloth and gelatin. The absorptivity of the gelatin layer is actually much greater than indicated because in the gas-cell fabric it is plasticized with polyglycerol, which is very hygroscopic. The paraffin coatings have very low

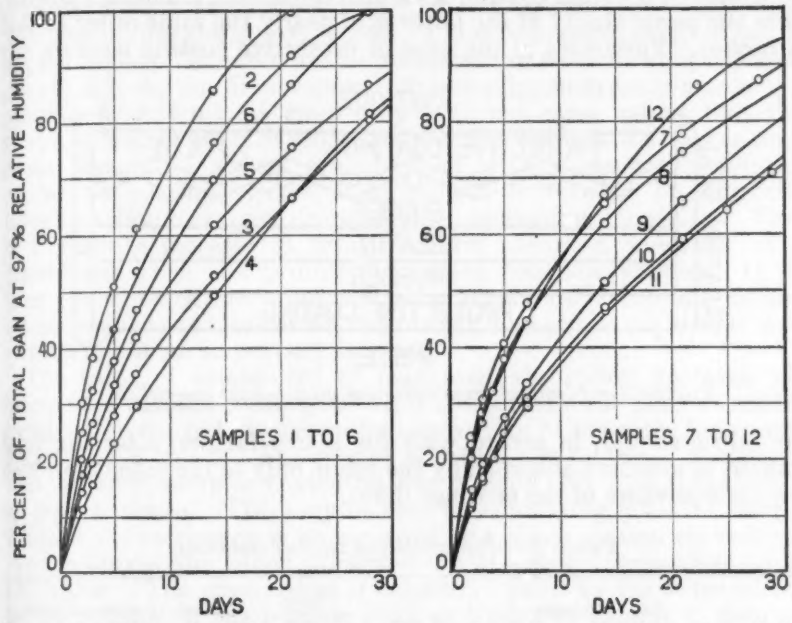

FIGURE 1.—*Rates of attainment of maximum absorption of moisture by gelatin-latex gas-cell fabrics.*

absorptive powers; varnishes have somewhat greater absorptivity, as may be seen from a comparison of the values given for samples 5 and 6 of set 1 in table 7 with the values for the remainder of the set.

TABLE 8.—*Moisture contents of materials at various relative humidities*

Material	Percentage of moisture held at relative humidity of—					
	13%	30%	50%	70%	90%	100%
Rubber [1]	0.17	0.28	0.60	0.74	0.99	----------
Gelatin (dry) [1]	1.01	2.80	4.92	7.6	11.4	----------
Cotton cloth [1]	2.99	4.56	6.7	9.6	13.5	----------
Balloon cloth, unmercerized [2]	2.6	4.3	5.6	7.6	12.5	27.1
Raw cotton [3]	2.7	4.1	6.0	8.2	13.9	----------

[1] R. E. Wilson and Tyler Fuwa, Ind. Eng. Chem. **14**, 916 (1922).
[2] G. M. Kline, J. Research NBS **14**, 72 (1935) RP758. Values are interpolated except at 100 percent relative humidity.
[3] A. R. Urquhart and A. M. Williams, J. Textile Inst. **15**, T138 (1924). Interpolated values.

Since the gelatin layer (the most hygroscopic) is in the center of the fabric, the permeabilities of the other layers to water vapor are also of importance. The layer of cloth offers no resistance to the entrance of moisture. Data on the permeability to moisture of rubber, paraffin, and varnishes, taken from information in the literature, are given in table 9 as "diffusivities"; this term is defined by Hermann [5] as "the number of grams of water which pass through a 1-cm cube in 1 hour under a vapor-pressure difference of 1 mm of mercury at a definite temperature." From the data shown, it would be expected that the rate of penetration of moisture into a paraffin-coated fabric would be governed more by the thickness of the coating than by the nature of the other materials. It would not appear to be so definitely controlled by a similar coating of varnish containing aluminum powder, since the permeability of the latter is of nearly the same order as that of rubber. Variations in the type of protective coating used on any

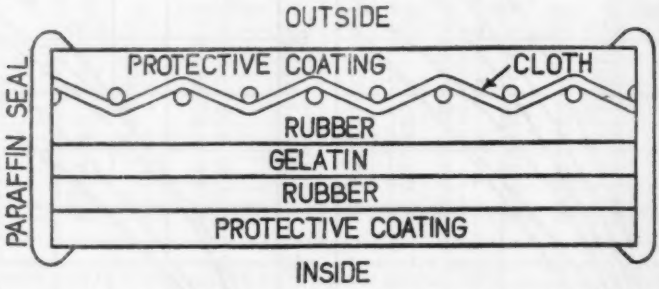

FIGURE 2.—*Idealized cross section of gelatin-latex gas-cell fabric.*

one fabric should, in accord with the above factors, alter the total amount of moisture absorbed by the fabric only to the extent to which the absorptivities of the coatings differ.

TABLE 9.—*Diffusivities of various materials*

Substance	Temp. °C	Diffusivity constants × 10⁴
Hydrocarbon wax [1]	25	0.1.
Soft vulcanized rubber [1]	25	2.3—2.8 (against vapor).
	25	4.6—5.1 (against liquid).
Do.[1]	25	7.0.
Clear varnishes [2]	27	15—60.
Varnishes containing aluminum powder [2]	27	6—10.

[1] D. B. Hermann, Bell Lab. Record **13**, 47 (1934).
[2] Caculated from measurements of permeability to water by J. D. Edward and S. F. Pickering, BS Sci. Pap. 387.
[3] Calculated from values for moisture impedance by R. I. Wray and A. R. Van Vorst, Ind. Eng. Chem. **25**, 842 (1933).

Two factors do, however, lower the total amount of moisture absorbed at high relative humidities—mold growth and leaching. Apparently, their effects are negligible at 21° C for relative humidities of less than 94 percent. Mold growth appears after periods of 2 weeks or longer on practically all samples which are exposed to relative humidities of 94 percent or more. Since the rate of loss in

[5] D. B. Hermann, Bell Lab. Record **13**, 47 (1934).

weight caused by this mold growth is increasing with time, and the rate of gain in weight of absorbed moisture is simultaneously decreasing, the sample soon begins to lose weight. The leaching effect is of a lesser magnitude, but at high humidities is probably a cause of irregularities. The moisture taken up by the fabric at these high humidities forms, after several weeks, droplets on the surface of the material. These droplets contain glycerol and gelatin leached from the fabric and, if accidentally lost during handling, cause slight apparent irregularities in the rate of change. Since some hygroscopic material is removed by such a loss, there is a tendency to lower the maximum absorption values.

A review of the results obtained with set 1 shows rather close correlation with the various gain and loss factors considered above. The maximum absorption values of the paraffined samples are all approximately the same until humidities are reached at which mold growth affects the final values. Apparently, increasing amounts of paraffin do not inhibit mold growth to the same extent that they retard the absorption of moisture, and the result is that lower maximum absorption values are obtained with increasing weights of protective coating. Since mold growth is favored by humidity, these maximum values decrease with increasing humidity. There is a definite increase in total moisture absorbed, however, at all humidities when the protective coating contains varnish. It has been found by Kline [6] that the same maximum values are reached by paraffined and uncoated fabrics at humidities at which mold growth is not an important factor.

The rates of attainment of maximum absorption decrease with increase of paraffin coating. This is illustrated at 97 percent relative humidity in figure 1, as shown by comparison of the rates for samples 1 and 2, or 3 and 4. The change in rate is not so great, however, as that between samples coated on one surface only and those coated on both surfaces. This may be seen by comparing rates for samples 2 and 3. The change is an expected one, since coating on only one surface leaves the other protected by the more permeable rubber film alone. The application of aluminum paint to the outer surface before putting on the paraffin coat, as shown by sample 5, does not decrease the rate. If aluminum varnish alone is used, the rate is greater than for a sample paraffined on both sides and approaches that of fabric paraffined on only one side; this is true despite the heavier coatings used when varnish is applied.

Similar effects are found in set 2 (samples 7 to 12). Here, because of the smaller amount of the hygroscopic gelatin-polyglycerol layer in the fabric, all the rates are lower, and the differences between them are less. For humidities at which attack by mold is not an important factor, the maximum absorption values are definitely less than for set 1, but at high humidities the lowered values obtained are of the same order. The approximate equality of the total moisture absorbed by the samples having various coatings is again shown, though here the increased value in the presence of varnish is not noticeable. The lowering of maximum absorption with increasing weight of coating, caused by the lack of inhibition of mold growth, is once more found at the higher humidities. The decrease in rate

[6] See p. 79 of reference 1.

of attainment of the maximum absorption with increased weight of paraffin is also evident in this set, as is the lowering of the rate by the application of the coating to both sides of the fabric. The application of aluminum paint before the paraffin in this set appears to have a slight beneficial effect (sample 11 of fig. 1), but when only aluminum varnish is used as a coating (sample 12) the rate becomes the highest of the set.

VI. CONCLUSIONS

(1) Increasing the thickness of the paraffin coating decreases the rate of absorption of moisture by gelatin-latex gas-cell fabric.

(2) Application of the paraffin coating to both surfaces of the fabric is much more effective than the application of an equal weight on one side only.

(3) Substitution of aluminum varnish for paraffin as a protective coating results in an increased rate of absorption of moisture by the fabric, though the coatings of varnish are much heavier.

(4) Except for the absorptivities of the coatings themselves, variation in type of coating does not appear to alter the total amount of moisture absorbed by the fabric at a given humidity.

(5) Reduction of the amount of gelatin plasticized with polyglycerol lowers the total amount of moisture absorbed by the fabric.

This investigation was sponsored by the Bureau of Aeronautics, U. S. Navy Department, and the results are published by permission of the chief of that Bureau.

The author wishes to acknowledge here the interest of the Bureau of Aeronautics during the course of this work, as well as the interest and suggestions of G. M. Kline of the National Bureau of Standards.

WASHINGTON, June 7, 1935.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP819

Part of Journal of Research of the National Bureau of Standards, Volume 15, August 1935

HYDROTHERMAL SYNTHESIS OF KAOLINITE, DICKITE, BEIDELLITE, AND NONTRONITE

By Raymond H. Ewell and Herbert Insley

ABSTRACT

Kaolinite was synthesized by heating coprecipitated Al_2O_3-SiO_2 gels and mixtures of Al_2O_3 and SiO_2 with water in a pressure bomb at 310° C. Similarly dickite was prepared by treating coprecipitated Al_2O_3-SiO_2 gels at 350° C and 365° C, beidellite from mixtures of Al_2O_3 and SiO_2 at 350° C and 390° C, and also from coprecipitated gels and kaolinite at 390° C. Nontronite was made by treating a coprecipitated Fe_2O_3-$2SiO_2$ gel at 350° C. Beidellite was formed in these experiments in the presence of soda by transport of SiO_2 in solution to the Al_2O_3 and reaction with Al_2O_3 in situ.

The products were identified by X-ray patterns. Their optical properties were also consistent with those of the natural minerals. The stability ranges of kaolinite, dickite, and beidellite probably occur in the order named, with increasing temperature. This relation between kaolinite and dickite is consistent with geological evidence as to their formation in nature.

CONTENTS

	Page
I. Introduction	173
II. Description of pure clay minerals used as comparison materials	174
1. Kaolin minerals—formula $Al_2O_3.2SiO_2.2H_2O$	174
2. Beidellite-nontronite minerals—formula $(Al_2O_3, Fe_2O_3).3SiO_2.nH_2O$	174
III. Preparation of materials	176
IV. Apparatus	177
V. General experimental procedure	178
VI. Synthesis of kaolinite and dickite	178
1. Experimental results	178
2. Discussion of results	179
3. Microscopical examination of products	179
VII. Synthesis of beidellite	179
1. Experimental results	179
2. Discussion of results	180
3. Microscopical examination of products	180
VIII. Mechanism of formation of beidellite	181
IX. Synthesis of nontronite	184
X. Hydrothermal treatment of other aluminum silicates	184
XI. Discussion	184
XII. Summary	185
XIII. References	185

I. INTRODUCTION

The formation of kaolin ($Al_2O_3.2SiO_2.2H_2O$) in nature and its possible synthesis in the laboratory have been a matter of much interest to geologists, chemists, and soil scientists for many years, and have been the subject of much speculation, but it has only been in the last decade that any successful experimental results have been obtained.

Schwarz and Brenner (1)[1] made coprecipitated gels of the composition Al_2O_3-$2SiO_2$ which were amorphous, but which after aging for 21 days at 20° C had a crystalline structure "related to that of kaolin" as shown by an X-ray pattern.

Van Nieuwenburg and Pieters (2), expressing doubts regarding the synthesis of kaolin claimed by Schwarz and Brenner, made a coprecipitated gel of composition Al_2O_3-$2SiO_2$-$2H_2O$ by a modification of Schwarz and Brenner's method and heated the gel in an autoclave for 12 days at 200 to 260 atmospheres steam pressure. This gave a product which was birefringent, had approximately the same mean index of refraction and density as kaolin, and from which a very small amount of Al_2O_3 was extracted by HCl. Their product was probably a kaolin mineral, but they did not make any X-ray patterns of it, and X-ray patterns constitute the only criterion of crystalline identity in such finely divided materials.

Noll (3) prepared a coprecipitated gel of composition Al_2O_3-$2SiO_2$-aq. by the method of Schwarz and Brenner, which was amorphous when first prepared and was still amorphous after standing 2 years in air. When this gel was heated with water in a pressure bomb for 5 days at 250 to 300 ° C (corresponding to 40 to 90 atmospheres steam pressure), there resulted a product which gave an X-ray pattern identical with that of kaolin. Noll made no reference to Van Nieuwenburg's work and had evidently not seen it. Noll made no attempt to distinguish between kaolinite, dickite, and nacrite, the three closely related kaolin minerals, although the paper by Ross and Kerr (4) describing the differences between them had been published at that time.

The present paper carries the work further and describes the synthesis of both kaolin and dickite in different temperature ranges, of beidellite, a related clay mineral, in still a third temperature range, and of nontronite, the iron analogue of beidellite.

II. DESCRIPTION OF PURE CLAY MINERALS USED AS COMPARISON MATERIALS

1. KAOLIN MINERALS—FORMULA $Al_2O_3.2SiO_2.2H_2O$

Washed kaolinite from Zettlitz, distributed as an international standard by the Ceramic Society of Czechoslovakia, dickite from the National Belle mine, Red Mountain, Colo., and nacrite from St. Peters Dome, Colo., were used as reference materials. These minerals have been thoroughly described by Ross and Kerr (4). X-ray patterns of these minerals show significant differences. Patterns of kaolinite and dickite are shown in figure 1.

2. BEIDELLITE-NONTRONITE MINERALS—FORMULA $(Al_2O_3,Fe_2O_3).3SiO_2.nH_2O$

Beidellite and nontronite are hydrous aluminum and iron silicates, respectively, with a SiO_2:R_2O_3 ratio equal to 3. Both are orthorhombic minerals and have the same X-ray patterns, except that the lines of nontronite are all shifted towards the zero beam relative to those of beidellite (fig. 2). They are therefore thought to be members of a series of isomorphous solid solutions. Both minerals

[1] Figures in parentheses here and throughout the text refer to the references at the end of this paper, p. 185.

have the same dehydration characteristics. Since they do bear this close relationship and since both end-members were synthesized in this work, they will be considered together.

Three beidellites were used as comparison materials:

(a) Montmorillonite from Otay, San Diego County, Calif.

(b) Beidellite from Beidell, Colo.

(c) Pink clay from pegmatite, San Diego County, Calif.

In spite of the differences in nomenclature and chemical composition (table 1), all 3 minerals gave the same X-ray patterns (fig. 2), except that the patterns of (a) and (c) have a few faint lines which do not appear in the pattern of (b) and all the lines in the pattern of (b) and (a) are shifted slightly toward the zero beam relative to (c). Also, by comparison with a photograph published by Hofmann, Endell, and Wilm (6), another montmorillonite (probably from Montmorillon, France), has the same pattern. In addition, (b) and (c) gave the same heating curves and the same dehydration curves.

TABLE 1.—*Chemical composition and optical constants for beidellites and nontronite*

Constituents	Al_2O_3·$3SiO_2$·$4H_2O$ (theoretical)	San Diego pink clay	Otay montmorillonite	Beidell beidellite	Sandy Ridge nontronite	Fe_2O_3·$3SiO_2$·$4H_2O$ (theoretical)
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
SiO_2	50.85	[a] 43.62	[b] 50.30	[c] 47.28	[d] 41.38	43.69
Al_2O_3	28.81	35.55	15.96	20.37	9.84	----------
Fe_2O_3	----------	.21	.86	8.68	27.47	38.83
CaO	----------	1.02	1.24	2.75	Trace	----------
MgO	----------	.19	6.53	.70	---do----	----------
K_2O	----------	.03	.45	Trace	---do----	----------
Na_2O	----------	.19	1.19	.97	---do----	----------
H_2O	20.34	18.88	23.61	19.72	21.35	17.48
Total	100.00	99.69	100.14	100.47	100.04	100.00
Optical Constants						
α	----------	[c] 1.495	[c] 1.492	[c] 1.494	1.54	----------
γ	----------	1.518	1.513	1.536	1.57	----------
$\gamma-\alpha$	----------	.023	.021	.042	.03	----------
2V	----------	----------	16 to 24°	Small	----------	----------

[a] W. T. Schaller, analyst, reference (5).
[b] J. E. Whitfield, analyst, reference (8).
[c] E. T. Wherry, analyst, reference (7).
[d] L. T. Richardson, analyst, private communication from C. S. Ross.
[e] Reference (8).

The nontronite used as a comparison material was from Sandy Ridge, N. C. It gave an X-ray pattern like that of the above beidellites, but with all the lines shifted toward the zero beam (fig. 2).

The true chemical composition of the minerals in this group is by no means as definitely known as in the case of the kaolin minerals. While the R_2O_3:SiO_2 ratios reported in the literature vary greatly (in beidellites from 1:2.1 to 1:3.6 (6, 7, 8, 9, 10); in nontronites from 1:2.5 to 1:3.5 (11, 12, 13, 14, 15, 16)), analyses of the purest materials indicate that 1:3 is the ratio most probably correct. Ratios of R_2O_3:H_2O also vary greatly (in beidellites from 1:3.5 to 1:5.6; in nontronites from 1:2 to 1:5.5), but 1:4 and 1:5 are mentioned most frequently as being the probably correct ratios.

As in the case of the zeolites, the dehydration curves of beidellite and nontronite are smooth curves without regions of rapid loss of water and the X-ray patterns do not change with loss of as much as three-fourths of the water. These data show that a large part of the water content of beidellite and nontronite is zeolitic in nature, and therefore has little meaning in a constitutional formula. Tammann and Grevemeyer (11) and Geilmann, Klemm, and Meisel (16) conclude that in nontronite one molecule of water is constitutional and is not lost until 300 to 500° C, whereas the other three or four molecules are lost below 200° C. The latter give no detailed data, and the data of the former, when plotted as a weight loss-temperature curve, offer small support for their conclusion. Our own dehydration experiments on beidellite and nontronite, and those of Larsen and Wherry (7) on biedellite, and of Larsen and Steiger (12) on nontronite fail to confirm this conclusion.

Ross and Shannon (8) conclude that at least some montmorillonites (including the one from Otay, Calif.) contain one molecule of constitutional RO (CaO + MgO), and Larsen and Steiger (12) believe the same to be true of some nontronites. However, this is certainly not a necessary part of the beidellite structure, as will be demonstrated in this paper.

To sum up this discussion, it may be stated that the probable formulas of the end members of the beidellite-nontronite series, whose synthesis will be described below, are $Al_2O_3.3SiO_2.nH_2O$ and $Fe_2O_3.3SiO_2.nH_2O$, where n is often 4 or 5 in natural minerals, but is variable as in zeolites.

Hofmann, Endell, and Wilm (6) have recently determined the crystal system of montmorillonite and a bentonite (localities not given) to be orthorhombic, a fact which several authors had previously surmised.

III. PREPARATION OF MATERIALS

Coprecipitated hydrogels of compositions $2Al_2O_3$-SiO_2, Al_2O_3-SiO_2, Al_2O_3-$2SiO_2$, Al_2O_3-$4SiO_2$ and Fe_2O_3-$2SiO_2$ were prepared by the method of van Nieuwenberg and Pieters (2). To a 4 percent solution of $Al_2(SO_4)_3.18H_2O$ in water, sufficient sodium silicate solution (containing 68 g of SiO_2 per liter) was added dropwise with constant stirring to give the desired molar ratios of alumina to silica. Then the solution was neutralized (to phenol red) by slowly adding 10 percent NaOH solution. The precipitate was filtered, dried at 110° C, ground to pass a no. 200 sieve, washed on a filter with hot water and again dried at 110° C. The Fe_2O_3-SiO_2 gel was similarly made from $FeCl_3.6H_2O$ and sodium silicate, using litmus paper as the indicator.

Schwarz and Brenner (1) and Schwarz and Walcker (17) found that an Al_2O_3:SiO_2 ratio of 1:5 was needed in the solutions to get a product Al_2O_3-$2SiO_2$. However, van Nieuwenburg and Pieters (2), using a slightly different procedure, found that the ratio in the precipitates was the same as the ratio in the solutions. Analyses of three of our 1:2 gel preparations gave Al_2O_3:SiO_2 ratios of 1:1.99, 1:1.90, and 1:1.88, respectively, which confirm van Nieuwenburg's findings. The other gels were not analyzed, but after the filtrates were evaporated to dryness on the steam bath they were found to be practically completely water-soluble in all cases. Any Al_2O_3, Fe_2O_3 or SiO_2 in this

neutral filtrate would have precipitated in insoluble form on evaporation.

Amorphous SiO_2 gel was prepared by precipitating sodium silicate solution with HCl. The precipitate was filtered, dried, and washed as described above.

Amorphous Al_2O_3 gel was prepared by precipitating $AlCl_3$ solution with NaOH in iced solution at the neutral point. The gelatinous precipitate was filtered, dried, and washed as described above. Precipitation by NaOH at higher temperatures, or precipitation by NH_3 at any temperature failed to give a completely amorphous precipitate.

All these gels were found to consist of clear angular, isotropic grains when examined under the microscope, and X-ray photographs showed they were all amorphous.

The presence of soda in these preparations was not suspected until late in the investigation. The 1:1.88 coprecipitated gel mentioned above was analyzed for soda and found to contain 0.65 percent of Na_2O.[2]

All the other gels involving the use of either sodium silicate or sodium hydroxide were found to contain small amounts of soda, as indicated by testing with zinc uranyl acetate. This soda undoubtedly had some effect on the results given in this paper, as will be discussed later.

γ-Al_2O_3, a crystalline modification of anhydrous Al_2O_3, was prepared by heating aluminum nitrate overnight at 750° C.

Böhmite, a crystalline modification of $Al_2O_3.H_2O$, was prepared by heating Al_2O_3 gel in an autoclave with water 18 hours at 350° C.

Each of these three forms of alumina was mixed with dried silica gel and also with finely powdered silica glass in proportions to give $Al_2O_3:SiO_2=1:2$. These mixtures were moistened and ground together in an agate mortar for 15 minutes and dried, and this process was repeated twice more, thus insuring uniform mixing and comparatively intimate contact.

IV. APPARATUS

A bomb, capable of withstanding 2,000 atmospheres pressure at 400° C, was constructed of tool steel according to the design of Morey and Fenner (18), with walls 12 mm thick and a capacity of 21 ml. The furnace used for heating the bomb was made of no. 16 nichrome wire wound on a mica-covered iron pipe and insulated with 4 inches of diatomaceous silica brick. The heating zone was twice as long as the bomb in order to insure uniform temperature distribution.

Temperatures were measured to ±1° C by means of a chromel-alumel thermocouple inserted in a well in the body of the bomb, and a portable potentiometer.

Identification of the crystalline compounds in the products was made by comparison of X-ray powder diffraction patterns, using either Mo $K\alpha$ radiation from a Coolidge tube and a camera of 20.8 cm radius, or Cu K radiation from an ion tube and a camera of 4.1 cm radius. Both cameras were arranged for taking direct comparison photographs of two materials on the same film.

[2] The percentage composition of this gel computed to a water-free basis was: SiO_2 52.19, Al_2O_3 47.13, Na_2O 0.92.

V. GENERAL EXPERIMENTAL PROCEDURE

The 5 coprecipitated gels and the 6 mixtures of alumina and silica were inclosed in covered platinum or porcelain capsules (3 ml and 2 ml capacity, respectively) and treated with water in the bomb. Most of the experiments were carried out in one of three temperature ranges: 305 to 315, 340 to 355, or 380 to 395° C. The temperature variation during each experiment was within ±5° C. The temperatures given in column 3 of tables 2 and 3 are estimated average temperatures, and the pressures in column 4 are the water-vapor pressures corresponding to these temperatures. At temperatures above the critical point of water (374° C and 218 atmospheres) the pressures were taken from the isothermal curves of van Nieuwenburg and Blumendal (19), the mass of water in the bomb being estimated roughly (an error of 10 percent in the estimate corresponds to a difference of only 3 atmospheres at 390° C). The times of heating given in column 2 of tables 2 and 3 are somewhat arbitrary and were not based on any predetermined rate of reaction.

After the heating period was completed, the bomb was removed from the furnace, and cooled in air; the products were then removed and dried at 110° C.

While principal dependence for identification was placed in the X-ray patterns, examinations of the products were also made with a petrographic microscope. In most cases the product was a heterogeneous mixture of amorphous and birefringent material, which made accurate determination of optical properties difficult, but in some cases good crystals were obtained.

VI. SYNTHESIS OF KAOLINITE AND DICKITE

1. EXPERIMENTAL RESULTS

The results are summarized in table 2, from which it is evident that, in general, kaolinite resulted from treatment of coprecipitated Al_2O_3-SiO_2 gels and admixtures of alumina and silica at 310° C, and dickite resulted from treatment of the coprecipitated gels at 345, 350, and 365° C.

X-ray patterns of the products of experiments 6 and 8 are reproduced in figure 1. The patterns of synthetic kaolinite and synthetic dickite show the same characteristic differences (indicated by arrows) as do the natural minerals.

TABLE 2.—*Synthesis of kaolinite and dickite*

Experiment	Starting material	Time of treatment	Temperature	Pressure	X-ray pattern of product
		Days	°C	atm	
1	Al_2O_3-$2SiO_2$ coprecipitated gel	300	[a]Room temp.	1	Amorphous.
2	do	300	Room temp.	1	Do.
3	do	100	[a] 95	1	Do.
4	do	100	95	1	Do.
5	do	11	250	39	Weak kaolinite.
6	do	7	310	97	Kaolinite.
7	do	7	345	157	Weak dickite.
8	do	11	345	157	Dickite.
9	do	10	365	202	Do.
10	Al_2O_3-$4SiO_2$ coprecipitated gel	10	350	167	Do.
11	Al_2O_3-SiO_2 coprecipitated gel	8	350	167	Dickite and böhmite.
12	$2Al_2O_3$-SiO_2 coprecipitated gel	10	350	167	Böhmite.
13	Al_2O_3gel+$2SiO_2$ gel (mixed)	10	310	97	Kaolinite.

[a] Unpurified gel aged in contact with original supernatant liquid, following Schwarz and Brenner (1). In all other experiments purified (but not soda-free) gels were treated with pure water.

Research Paper 819

Journal of Research of the National Bureau of Standards

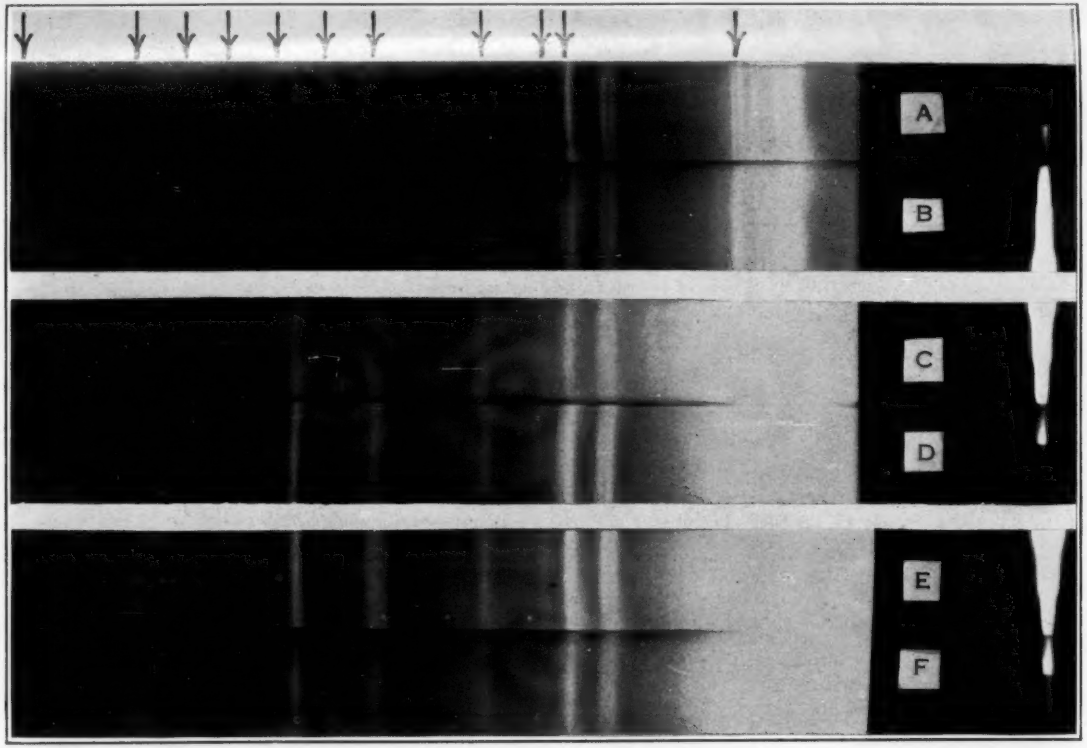

FIGURE 1.—*X-ray patterns of natural and synthetic kaolinite and dickite.*

A, Red Mountain dickite *B*, zettlitz kaolinite; *C*, synthetic dickite (experiment 6); *D*, zettlitz kaolinite; *E*, Red Mountain dickite; *F*, synthetic kaolinite (experiment 8).

FIGURE 2.—*X-ray patterns of natural and synthetic beidellite and nontronite.*

A, Montmorillonite from Otay, Calif.; *B*, beidellite from Beidell, Colo.; *C*, "pink clay" from San Diego, Calif.; *D*, synthetic beidellite (experiment 14); *E*, beidellite from kaolinite (experiment 25); *F*, zettlitz kaolinite; *G*, nontronite from Sandy Ridge, N. C.; *H*, synthetic iron silicate product.

2. DISCUSSION OF RESULTS

Schwarz and Brenner (1) claimed that, while newly precipitated Al_2O_3-SiO_2 gels were amorphous, after aging 21 days in contact with the original mother liquor, one gel developed a crystalline structure which was shown by X-rays to be "similar to or at least closely related to that of kaolin", but they gave no reproduction of their X-ray pattern or spacing data. Our experiments 1 and 2, aged at room temperature in water and in contact with the mother liquor, respectively, for periods greatly exceeding those used by Schwarz, fail to confirm his results. Furthermore, experiments 3 and 4, performed at 95° C, where any crystallization process would be expected to proceed more rapidly, failed to give any evidence of crystallinity. In addition, Schwarz states that all the alumina in his product was soluble in HCl and that the product lost most of its water below 260° C, both of which properties are unlike those of kaolinite.

Gels with a higher ratio of Al_2O_3 to SiO_2 than 1:2 may contain böhmite as is shown by experiments 11 and 12. Experiment 13 shows that kaolinite may also be formed from mixtures of the amorphous oxides although not in as close contact as in the coprecipitated gels (see other results with mixtures of the oxides in section VII).

3. MICROSCOPICAL EXAMINATION OF PRODUCTS

Microscopical examination of the synthetic kaolinite-dickite products showed them to be very heterogeneous and finely divided, and no accurate measurements of optical properties could be made. However, the following optical characters were observed—

Experiments 1, 2, 3, 4. Clear, isotropic grains, no perceptible birefringence.

Experiment 5. Very slight birefringence, mean index of refraction about 1.51.

Experiment 6. Somewhat more birefringent than 5, index of a few grains higher than 1.56 but most were lower than 1.56.

Experiments 7, 8, 9. Moderate birefringence, mean index about 1.56.

Experiment 10. About the same birefringence as 7, mean index about 1.52.

Experiment 12. High birefringence, mean index about 1.62.

The birefringence and mean index of the products of experiments 7, 8, and 9 agree with those of dickite. The low mean index of 10 is probably explained by the excess silica and the high birefringence and high mean index of 12 are due to the large amount of böhmite present.

VII. SYNTHESIS OF BEIDELLITE

1. EXPERIMENTAL RESULTS

In general beidellite was formed by treatment of mixtures of alumina and silica at 350 and 390° C, and of coprecipitated gels and of kaolinite at 390° C. The results are summarized in table 3. Experiments 24 to 28 are inserted to show how the individual component oxides used in experiments 14 to 21 behave when treated alone under the same conditions.

A, Montmorillonite from Otay, Calif.; *B*, beidellite from Beidell, Colo.; *C*, "pink clay" from San Diego, Calif.; *D*, synthetic beidellite (experiment 14); *E*, beidellite from kaolinite (experiment 20); *F*, soft clay kaolinite; *G*, bentonite from Sandy Ridge, N. C.; *H*, synthetic iron silicate product.

TABLE 3.—*Synthesis of beidellite*

Experiment	Starting material	Time of treatment	Temperature	Pressure	X-ray pattern of product
		Days	°C	atm	
14	Al_2O_3 gel+2SiO_2 gel	12	350	167	Beidellite.
15	Al_2O_3 gel+2SiO_2 glass	12	350	167	Beidellite+faint böhmite.
16	γ-Al_2O_3+2SiO_2 gel	18	350	167	Beidellite.
17	γ-Al_2O_3+2SiO_2 glass	18	350	167	Do.
18	Böhmite+3SiO_2 gel	9	350	167	Böhmite+beidellite.
19	Böhmite+3SiO_2 glass	9	350	167	Do.
20	Al_2O_3 gel+2SiO_2 gel	10	390	260	Beidellite.
21	γ-Al_2O_3+2SiO_2 gel	10	390	260	Do.
22	Al_2O_3-2SiO_2 coprecipitated gel	14	390	260	Do.
23	Zettlitz kaolin	14	390	260	Do.
24	Al_2O_3 gel	5	350	167	Böhmite.
25	γ-Al_2O_3	5	350	167	Do.
26	Böhmite	5	350	167	No change.
27	SiO_2 gel	5	350	167	Cristobalite.
28	SiO_2 glass	10	350	167	No change.

2. DISCUSSION OF RESULTS

Patterns of the products of experiments 14 and 23 are reproduced in figure 2. Patterns of 15, 16, 17, 20, and 21 were identical with that of 14, except for the presence of a few faint lines of böhmite in the pattern of 15. The differences between the patterns of beidellite and kaolinite are quite pronounced and leave no doubt as to the identity of these synthetic beidellite products.

The pattern of 23 is that of beidellite, except for the presence of 3 or 4 faint lines which are not present in the pattern of pure beidellite and which have not been accounted for, and is profoundly different from that of the Zettlitz kaolin, from which it was made. This change in crystal structure is also apparent microscopically, the birefringence having increased from 0.006 (value for kaolinite) to more than 0.030. The pattern of 22 was identical with that of 23.

As will be shown in section VIII, the products of experiments 18 and 19 would probably have gone completely to beidellite if given a longer time. Experiments 14 to 19 show no significant difference in the reactivity of SiO_2 gel and SiO_2 glass.

3. MICROSCOPICAL EXAMINATION OF PRODUCTS

The synthetic beidellite products were much better crystallized and their optical properties could be more accurately determined than in the case of the synthetic kaolin minerals. The indices of refraction of the products were all higher than those of natural beidellite (see table 1) and, furthermore, beidellites formed in different experiments at the same temperature varied in indices. These variations might be due to variations in water content or to variations in Al_2O_3:SiO_2 ratio. Examinations of partially dehydrated natural beidellite showed qualitatively that the indices do vary with water content. Larsen and Steiger (12) found that the indices of nontronite increased with loss of H_2O, and beidellite would be expected to behave similarly.

The synthetic beidellites consisted principally of platy material with low birefringence when viewed normal to the cleavage and moderately high birefringence (0.020 to 0.030) when viewed parallel to the cleavage. The plates sometimes occurred as spherulitic

aggregates. Extreme variations in indices of refraction were: α=1.51 to 1.545 and γ=1.53 to 1.575. When the plates stood on edge they gave the appearance of birefringent needles of parallel extinction and positive elongation, and provided the best means of determining the maximum and minimum indices.

Besides the platy materials, there were also aggregates of finely divided material presenting a mosaic appearance, partly crystalline (probably beidellite like the platy material) and partly amorphous. These particles usually had birefringent margins which were convenient for determining indices. The appearance of some of the products was strikingly like that of some natural beidellites, montmorillonites and bentonites.

The results of microscopical examination of products of some of the experiments were as follows:

Experiments 16 and 17. Principally imperfect spherulites and some plates with α=1.52, γ=1.54.

Experiment 14. More heterogeneous than 16, many plates with α=1.51, γ=1.53.

Experiment 15. Most like natural beidellite in appearance, many plates with α=1.53, γ=1.55.

Experiment 23. Large masses of highly birefringent plates with α=1.545, γ=1.575, quite different in appearance and index from the original kaolinite.

Experiment 22. Mosaic particles with mean index of 1.56 and moderate birefringence. There were no particles large enough to measure indices in different directions.

Since experiments 23 and 22 have identical X-ray patterns and their mean indices are consistent, they are probably the same material.

VIII. MECHANISM OF FORMATION OF BEIDELLITE

It will be noted from tables 2 and 3 that dickite was formed from coprecipitated gels, and beidellite from alumina-silica mixtures at the same temperature, namely, 345 to 350° C. This difference in resulting product is probably due to the greater intimacy of contact between the alumina and silica in the gels than in the mixtures. That there is sufficiently intimate contact between alumina and silica in coprecipitated gels to bring molecular forces into play has been indicated by recent work of the present authors (20). Since there is this close molecular contact in the gels, it is not difficult to imagine a mechanism of direct combination of alumina, silica, and water to form dickite and kaolinite.

However, since the alumina and silica could hardly have been in such close contact in the mixtures of experiments 14 to 21 in spite of the thorough grinding, it seemed interesting to try to discover the mechanism of beidellite formation in these experiments. Three possible mechanisms suggest themselves:

(a) Solution of SiO_2 and its transport through the liquid phase to the Al_2O_3 where the reaction takes place between SiO_2 in solution, and solid Al_2O_3.

(b) Solution of Al_2O_3 and its transport through the liquid phase to the SiO_2, where the reaction takes place between Al_2O_3 in solution and solid SiO_2.

(c) Solution of both Al_2O_3 and SiO_2 and reaction in solution with precipitation of beidellite.

In order to test these hypotheses, six experiments were performed. In each experiment about ½ g of either dried Al_2O_3 gel or SiO_2 gel was placed in the bottom of the bomb. A smaller amount (about $\frac{1}{20}$ g) of the other oxide was placed in a platinum capsule, which was then filled with water and covered with a platinum foil cap tightly wired on. The capsule was placed in the bomb on top of the first-mentioned oxide and water added to cover the capsule. The cover of the capsule was wired on so tightly that no convection currents could possibly carry the outside oxide into the capsule, and therefore any transport of either oxide would have to be made by means of diffusion of dissolved material. After each experiment, X-ray patterns were made of the material in the capsule. The results are summarized in table 4.

TABLE 4

Experiment	Oxide in capsule	Oxide outside capsule	Time	Temperature	Pressure	X-ray pattern of material in capsule	X-ray pattern of material outside capsule
				°C	atm.		
29	Al_2O_3 gel	SiO_2 gel	12 days	355	178	Beidellite	Cristobalite.
30	SiO_2 gel	Al_2O_3 gel	10 days	355	178	(See next paragraph of text.)	Böhmite.
31	do	None	7 days	355	178	do	None.
32	Al_2O_3 gel	SiO_2 gel	12 days	385	248	Beidellite	Cristobalite.
33	do	do	4 hours	[a] 385	248	Böhmite	Do.
34	Product of 33 (in capsule).	None	10 days	355	178	do	None.

[a] The bomb was removed when the temperature first reached 385° C, 4 hours after the beginning of heating.

X-ray patterns of the products inside the capsule from experiments 29 and 32 were identical with that of 14 shown in figure 2. In experiment 30 most of the SiO_2 (at least 75 percent) had disappeared from the capsule. The small amount that was left was yellow-brown in color, presumably due to iron. It gave an X-ray pattern different from patterns of both beidellite and cristobalite, and which did not correspond to any known form of silica, alumina, aluminum silicate, iron oxide, or iron silicate. Microscopical examination showed it to be a yellowish, crystalline material with an index (about 1.67) too high for a hydrated aluminum silicate. The same result was obtained in experiment 31 when there was no Al_2O_3 in the bomb.

The evidence of experiments 29, 30, and 31 shows that beidellite must have been formed in experiments 14 to 21 by transport of SiO_2 in solution, and not by transport of Al_2O_3, and that therefore hypothesis (a) is the correct one.

Microscopical examination of the products inside the capsule from experiments 29 and 32 showed them to consist entirely of good spherulites of birefringent plates (fig. 3) with mean index of 1.53 and birefringence of at least 0.020. At the center of each spherulite there was a small core of a material with higher index. In the light of experiment 33, this core is undoubtedly böhmite (index about 1.65).

Research Paper 819

Journal of Research of the National Bureau of Standards

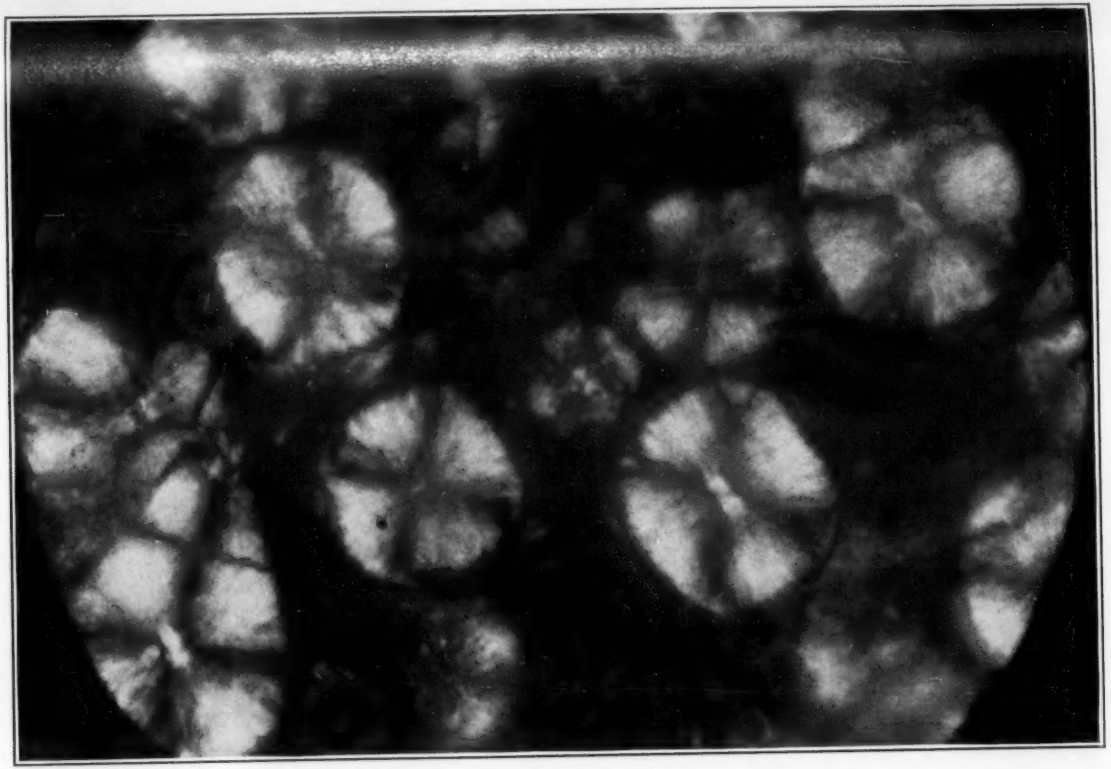

FIGURE 3.—*Spherulites of synthetic beidellite from experiment 29.*

Crossed nicols. Magnification 1,400 ×.

UNIV. OF MICH.

The absence of böhmite lines in the X-ray pattern is due to the small amount of böhmite (less than 2 percent) in the spherulites. Formation of böhmite in these experiments is evidently an intermediate step in the formation of beidellite, and is probably completed before the slower process of solution of the silica and its diffusion and reaction with the alumina has even reached a steady state.

The product of experiment 32 was identical with that of 29, although the former experiment was carried out above the critical temperature of water where there is no liquid phase (or rather, where the differences between the liquid and vapor phases become indeterminate). These two experiments indicate a transport of silica through the gaseous as well as the liquid phase. Van Nieuwenburg and Blumendal (21, 22, 23, 24) and Gillis (25) have given evidence that many silicates may be formed pneumatolytically by transport of silica through the compressed gaseous phase, while Morey (26) was unable to duplicate their results. Morey concluded that the transport of silica in their experiments must have taken place through the liquid phase in the heating interval before the temperature exceeded the critical point. Our experiments 33 and 34 were performed to test this conclusion. Experiment 33 shows that no beidellite was formed up to the time when the critical temperature was exceeded. The product of experiment 34 shows further that 33 did not contain any appreciable amount of silica which had been transported through the liquid phase but had not yet reacted with the alumina, since no beidellite was observed in 34. It may, therefore, be concluded that the beidellite in 32 was formed by transport of silica through the dense gaseous phase. One would hardly expect a discontinuity in the solubility of silica in water at the critical temperature, since the properties of water (which determine its solvent power) undergo no discontinuity at that temperature.

The presence of soda in the materials used, mentioned in section III, may have had some effect on these experiments. In order to test this, some new soda-free gels were prepared. A new silica gel was prepared by boiling a commercial silica gel in concentrated nitric acid; the product gave a residue of 0.05 percent nonvolatile with hydrofluoric acid. A new alumina gel was prepared by precipitating aluminum chloride with ammonia instead of sodium hydroxide; this gel was not completely amorphous as was the gel precipitated with sodium hydroxide in iced solution, but gave a faint diffuse X-ray pattern of böhmite. Both these preparations were indicated to be free from soda by testing with zinc uranyl acetate. When experiments 27, 29, and 32 were repeated using these gels, the results were not the same as given above. The silica gel did not change to cristobalite in any of the experiments; in 29 and 32 the material inside the capsule was böhmite instead of beidellite. These results show that soda was a necessary factor in the formation of beidellite in the experiments reported in this paper. Probably the soda accelerates the reaction by increasing the solubility of the silica (and possibly that of the alumina also). The presence of soda in the coprecipitated gels probably was a factor in the formation of kaolinite and dickite in experiments 1 to 13, but whether it was a necessary factor would be hard to prove since it would be difficult to prepare such a coprecipitated gel completely free of soda.

IX. SYNTHESIS OF NONTRONITE

The dried Fe_2O_3-$2SiO_2$ gel was treated in the bomb for six days at 340 to 350° C. The resulting product was a mixture of a red and a green material. When treated with hot 6*N* HCl the red material (hematite) quickly dissolved, leaving the bright green material. This was washed and dried at 110° C.

The X-ray pattern of the green material (fig. 2) showed lines corresponding to each line of natural nontronite, plus several extra lines which did not correspond to any known form of iron oxide or silica.

Chemical analysis of the green material dried at 110° C gave: Fe_2O_3 41.6, SiO_2 53.5, H_2O 4.9 percent, corresponding to a molar ratio of Fe_2O_3:3.43 SiO_2:1.04 H_2O.

Microscopical examination of the green material showed the presence of two intimately associated phases in about equal amounts:

1. Small needles (or plates on edge) with $\gamma=1.63$, $\alpha=1.60$, positive elongation, parallel extinction.

2. Large masses of weakly birefringent green material with no extinction position.

Substance 1 is probably nontronite since its optical properties are consistent with those of natural nontronite (Larsen and Steiger (12) give variations of the β index of nontronite as 1.585 for 13.06 percent of H_2O to 1.69 for 1.81 percent of H_2O), and the extra lines in the X-ray pattern must be ascribed to substance 2. The nature of substance 2 was not investigated further. It is probably a hydrated iron silicate, and from comparison of the above chemical analysis with the formula of pure nontronite ($Fe_2O_3:SiO_2$ =1:3), substance 2 must have $SiO_2:Fe_2O_3$ greater than 3.5, possibly 4.

A ground mixture of Fe_2O_3 and SiO_2 gel was also treated in the bomb, but only hematite and cristobalite resulted.

X. HYDROTHERMAL TREATMENT OF OTHER ALUMINUM SILICATES

Andalusite, cyanite, sillimanite (all of formula $Al_2O_3.SiO_2$), mullite ($3Al_2O_3.2SiO_2$), pyrophyllite ($Al_2O_3.4SiO_2.H_2O$) and orthoclase ($K_2O.Al_2O_3.6SiO_2$) were heated in the bomb for 10 days at 350° C. No change was observed in any case.

XI. DISCUSSION

The data in this paper pertain to the system Al_2O_3-SiO_2-H_2O. Data such as these are difficult of accurate interpretation since amorphous solid phases are present in the final products and conditions are such that equilibrium may not have been reached. Furthermore there are surface forces in the coprecipitated gels which make the results of those experiments uncertain in their relation to true equilibrium. Thus it can be concluded from these data only that the stability ranges of kaolinite, dickite, and beidellite probably occur in that order with increasing temperature.

Ross and Kerr (4) have summarized the geological evidence pertaining to the formation of the kaolin minerals and conclude that kaolinite is the result of low-temperature weathering processes and that dickite and nacrite are formed by hydrothermal processes at

higher temperatures. This conclusion is consistent with the relative temperatures of formation of kaolinite and dickite given in this paper.

The conditions of formation of beidellite in nature are not well known, but at least some bentonites (a rock containing beidellite) seem to have been formed by low-temperature weathering of volcanic glass. This is seemingly in opposition to our data.

Nacrite and pyrophyllite were not observed in any of the products, so their regions of stability are either outside the range studied or occupy a narrow range which was overlooked.

XII. SUMMARY

Four clay minerals were synthesized by treating coprecipitated hydrogels and mixtures of oxides with water in a pressure bomb at high temperatures as follows:

1. Kaolinite from coprecipitated Al_2O_3-SiO_2 gels and mixtures of Al_2O_3 and SiO_2 at 310° C.
2. Dickite from coprecipitated Al_2O_3-SiO_2 gels at 350° C and 365° C.
3. Beidellite from mixtures of Al_2O_3 and SiO_2 at 350 and 390° C and coprecipitated gels and kaolinite at 390° C.
4. Nontronite from a coprecipitated Fe_2O_3–$2SiO_2$ gel at 350° C.

The products were identified by X-ray powder patterns. Their optical properties were also consistent with the natural minerals.

Beidellite was formed in these experiments in the presence of soda by transport of SiO_2 in solution to the Al_2O_3 and reaction with the Al_2O_3 in situ. This is true both below and above the critical temperature of water. In the absence of soda this reaction did not take place.

The stability ranges of kaolinite, dickite, and beidellite probably occur in the order named with increasing temperature. This relation between kaolinite and dickite is consistent with geological evidence pertaining to their formation in nature.

Acknowledgment is made to Dr. C. S. Ross, of the United States Geological Survey, and to Dr. W. F. Foshag, of the United States National Museum, for kindly supplying samples of pure clay minerals used in this investigation.

XIII. REFERENCES

(1) R. Schwarz, and A. Brenner, Ber. deut. chem. Ges. **56B**, 1433–7 (1923).
(2) C. J. van Nieuwenburg, and H. A. J. Pieters, Rec. trav. chim. **48**, 27–36 (1929).
(3) W. Noll, Naturwissenschaften **20**, 366 (1932).
(4) C. S. Ross, and P. F. Kerr, U. S. Geol. Survey Professional Paper 165–E (1930).
(5) W. T. Schaller, U. S. Geol. Survey Bul. 262, p. 121.
(6) U. Hofmann, K. Endell, and D. Wilm, Z. Krist. **86**, 340–8 (1933).
(7) E. S. Larsen and E. T. Wherry, J. Wash. Acad. Sci. **7**, 208–17 (1917).
(8) C. S. Ross and E. V. Shannon, J. Am. Ceram. Soc. **9**, 77–96 (1926).
(9) S. B. Hendricks, and W. H. Fry, Soil Sci. **29**, 457–79 (1930).
(10) P. F. Kerr, Econ. Geol. **26**, 153–68 (1931).
(11) G. Tammann, and C. F. Grevemeyer, Z. anorg. Chem. **135**, 197–200 (1924).
(12) E. S. Larsen, and G. Steiger, Am. J. Sci. **15**, 1–19 (1928).

(13) I. Parga-Pondal, Arquivos Seminario Estud. Galegos, p. 9–14 (1929); Chem. Abs. **24**, 1059 (1930).
(14) W. Noll, Chem. Erde **5**, 373–84 (1930).
(15) I. J. Mickey, Centr. Mineral. Geol. **1930** [A], 293–303.
(16) W. Geilmann, W. Klemm, and K. Meisel, Naturwissenschaften **20**, 639–640 (1932).
(17) R. Schwarz, and W. Walcker, Z. anorg. Chem. **145**, 304–10 (1925).
(18) G. W. Morey, and C. N. Fenner, J. Am. Chem. Soc. **36**, 215 (1914).
(19) C. J. van Nieuwenburg, and H. B. Blumendal, Rec. trav. chim. **51**, 707–14 (1932).
(20) H. Insley, and R. H. Ewell, J. Research NBS **14**, 615–27 (1935) RP792.
(21) C. J. van Nieuwenburg, and H. B. Blumendal, Rec. trav. chim. **49**, 857–61 (1930).
(22) C. J. van Nieuwenburg, and H. B. Blumendal, Rec. trav. chim. **50**, 129–38 (1931).
(23) C. J. van Nieuwenburg, and H. B. Blumendal, Rec. trav. chim. **50**, 989–96 (1931).
(24) C. J. van Nieuwenburg, and H. B. Blumendal, Rec. trav. chim. **53**, 476 (1934).
(25) J. Gillis, Natuurw. Tijdschr. **15**, 153–4 (1933).
(26) G. W. Morey, Trans. Am. Geophys. Union, 13th Annual Meeting, 1932 p. 269–70.

WASHINGTON, January 8, 1935.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP820

Part of Journal of Research of the National Bureau of Standards, Volume 15, August 1935

FRACTIONATION OF THE ISOTOPES OF OXYGEN IN A COMMERCIAL ELECTROLYZER—*A CORRECTION*

By Edgar R. Smith and Mieczyslaw Wojciechowski [1]

In a previous publication,[2] there was reported an investigation of the electrolytic fractionation of the isotopes of hydrogen and of oxygen under the conditions prevailing in a commercial hydrogen-oxygen electrolyzer. It was found that after an amount of water approximately equal to 10 times the volume of a commercial alkaline cell has been electrolyzed, a steady state is closely approached in which no further isotopic fractionation occurs. In this state the gases evolved have the isotopic composition existing in the water repeatedly added to the cell. A sample of this residual "equilibrium" water was subjected to an isotopic analysis consisting in successive treatments with dry ammonia gas, to normalize isotopically its hydrogen content, until the density had apparently decreased to a constant value. However, an error has now been found in the calculation of one of the densities, which made the results appear to agree after the third and fourth ammonia treatments. This error was discovered in an effort to account for the discrepancy between the results reported and those obtained recently at Princeton University on the electrolytic concentration of oxygen isotopes.[3] The purpose of this paper is to report the error and also to report a redetermination of the isotopic composition of "equilibrium" water from alkaline electrolyzers.

For this new analysis, a sample of water was obtained from the cells of the Southern Oxygen Co., South Washington, Va., and was first reduced in our electrolyzer to about half the original volume, because the equilibrium water from the Southern Oxygen Co. has been shown to be somewhat less heavy than corresponds to true equilibrium.[4] After this preliminary treatment, the water was distilled from the potassium hydroxide and treated with ammonia gas as follows. A sample of about 500 ml was placed in a liter flask immersed in a bath of acetone and carbon tetrachloride contained in in a 4-liter dewar tube. "Anhydrous" ammonia gas was passed over solid potassium hydroxide to insure dryness and then through a safety trap into the sample until the volume of the sample was approximately doubled and the flask was filled. Meanwhile the sample was kept just at its freezing temperature by additions of solid carbon dioxide to the bath. A reflux condenser was then attached to the flask and the sample boiled until its volume was reduced to the original size. After nine such treatments, the sample was freed from ammonia and other nonaqueous impurities, and the difference between its density and that of purified normal water was measured at

[1] Guest worker from the Polytechnic Institute, Warsaw, Poland.
[2] E. W. Washburn, E. R. Smith, and F. A. Smith, J. Research NBS **13**, 599 (1934) RP729.
[3] P. W. Selwood, H. S. Taylor, J. A. Hipple, Jr., and W. Bleakney, J. Am. Chem. Soc. **57**, 642 (1935).
[4] See footnote 2.

25° C by the use of differential pycnometers described in a previous paper.[5] The difference in density was found to be 11.1 ppm. The sample was then submitted to two more ammonia absorptions and after purification was found to be 11.3 ppm heavier than normal water, the two values agreeing well within the precision of 1 ppm of the measurements and showing that the sample had attained the same composition with respect to hydrogen as the ammonia. The latter was shown to have normal isotopic composition by comparing the density of ordinary purified water with ordinary water which was twice treated with ammonia in the manner just described, before purification. The difference in density was less than 1 ppm.

When the corrected value of 11 ppm is used for the increase in density caused by heavy oxygen, the electrolytic fractionation factor for the hydrogen isotopes becomes 3.5 instead of the value 2.4 reported previously.

Assuming the O^{17} isotope to be negligible in amount, the separation factor, α, for the oxygen isotopes, defined as the ratio of O^{18}/O^{16} in the electrolyte to that in the oxygen gas evolved, can be computed from the composition of equilibrium water as follows. In the normal oxygen evolved from equilibrium water $(O^{18}/O^{16})=1/500$ while in the electrolyte $(O^{18}/O^{16})=(1+11/220)1/500$ and $\alpha=(1+11/220)/1=1.05$. It is interesting to compare the actual decrease in density of the water formed by combining with normal hydrogen the first electrolytic oxygen from normal water with the decrease computed with the aid of this separation coefficient. The computed decrease is $220(1-1/1.05)$ $=10.6$ ppm as compared with the measured decrease of 13.2 ppm. The agreement is adequate since a small change in α results in a relatively large change in the calculated decrease in density. For example, if $\alpha=1.06$ the calculated decrease in density is 12.5 ppm. The value of 1.05 for α during the initial stages of electrolysis is larger than has recently been reported,[6], [7] but is in fair agreement with the fractionation factor of 1.04 calculated from the results of Green and Voskuyl.[8]

SUMMARY

The electrolytic fractionation factor for O^{16} and O^{18}, defined as the ratio of O^{18}/O^{16} in the electrolyte to the same ratio in the oxygen gas evolved by electrolysis, has been found to be 1.05. An isotopic analysis of "equilibrium water" from a commercial electrolyzer indicates that about 11 ppm of the increase in density is a result of enrichment in heavy oxygen, and the value of 31 ppm previously reported is incorrect.

One of us [9] wishes to express gratitude to the Polish Fundusz Kultury Narodowej in Warsaw for financial aid.

WASHINGTON, June 4, 1935.

[5] E. W. Washburn and E. R. Smith, BS J. Research 12, 305 (1934) RP656.
[6] See footnote 3.
[7] H. L. Johnston, J. Am. Chem. Soc. 57, 484 (1935).
[8] C. H. Green and R. J. Voskuyl, J. Am. Chem. Soc. 56, 1649 (1934).
[9] M. Wojciechowski.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP821

Part of Journal of Research of the National Bureau of Standards, Volume 15, August 1935

ANALYSIS OF TEXTILES FOR CELLULOSE-ACETATE RAYON, SILK, REGENERATED-CELLULOSE RAYON, COTTON, AND WOOL

By Ralph T. Mease and Daniel A. Jessup

ABSTRACT

A quantitative method for the determination of cellulose-acetate rayon, silk, regenerated-cellulose rayon, cotton, and wool in textiles containing two or more of these fibers is described. The textile is first extracted with carbon tetrachloride, and desized with a starch and protein hydrolyzing enzyme and by washing. Acetate rayon (acetone-soluble type) is removed with acetone, and silk and regenerated-celulose rayons with solutions of calcium thiocyanate of specific gravity 1.20 and 1.36, respectively. Cotton and wool are determined either by removal of cotton with aluminum chloride and heat to leave the wool, or by dissolving the wool in potassium-hydroxide solution to leave the cotton. The method gives the percentage of each of the fibers present in the mixture to within 2 percent of the weight of the specimen analyzed.

CONTENTS

	Page
I. Introduction	189
II. Purification of fibers	190
III. Action of reagents on purified fibers	190
IV. Procedure for the analysis of fiber mixtures	194
1. Preparation of specimen for analysis	194
2. Drying and weighing of specimen	194
3. Determination of total sizing, finishing, and other nonfibrous materials	195
4. Determination of cellulose-acetate rayon	195
5. Determination of silk	195
6. Determination of regenerated-cellulose rayon	196
7. Determination of wool protein	196
8. Alternative method for determination of cotton	196
V. Analysis of specimens of known composition	197

I. INTRODUCTION

The study of methods for the analysis of textiles composed of cotton and wool [1] has been extended to include mixtures containing, in addition to these fibers, cellulose-acetate rayon [2] (acetone-soluble type), silk, and regenerated-cellulose rayon, or any two or more of these fibers.

The general procedure in the analysis of fiber mixtures is to eliminate sizing, finishing, and other nonfibrous materials from the mixture and then to remove the different kinds of fibers, one at a time, by suitable reagents. The action (on purified samples of each kind of

[1] BS J. Research **12**, 75 (1934) RP635.

[2] The use of the terms rayon, cellulose-acetate rayon, cuprammonium rayon, nitrocellulose rayon, and viscose rayon used in this paper is in accordance with definitions given in Tentative Definitions and Terms Relating to Textile Materials, Am. Soc. Testing Materials designation D123-33T. Proc. Am. Soc. Testing Materials, **33**, part I, 944 (1933).

fiber) of a typical desizing treatment and of the reagents which appeared to be useful for the separation of the kinds of fibers, was determined in the present work. Mixtures of known composition were analyzed in order to demonstrate the practicability of a proposed standard procedure and to indicate the accuracy attainable. The results are given in this paper.

II. PURIFICATION OF FIBERS

The silk was prepared from thrown silk by immersion for 20 to 30 minutes in a boiling 0.2-percent solution of neutral soap. The silk was rinsed with successive portions of hot distilled water until the rinse water appeared to be free of soap, immersed for 20 minutes in a boiling 0.1-percent solution of sodium carbonate, rinsed, dried, extracted for 6 hours in a soxhlet extraction apparatus with ethyl alcohol, and then for 6 hours with ether, air-dried, washed with warm water, and dried.

The cellulose-acetate rayon and the wool were prepared from yarns in the same manner, except that the temperature of the soap and sodium-carbonate solutions used for the wool was kept at approximately 70° C, and the cellulose-acetate rayon was not extracted with alcohol and ether.

The regenerated-cellulose rayons used in this study included the following four types: nitrocellulose, cuprammonium, ordinary viscose, and viscose manufactured by the Lilienfeld [3] process. These fibers were prepared by extracting successively, for periods of 6 hours each, with ethyl alcohol, diethyl ether, and with a 1-percent aqueous solution of potassium hydroxide; washing with dilute acetic acid, then with distilled water, and drying.

III. ACTION OF REAGENTS ON PURIFIED FIBERS

Several organic solvents for grease, oils, and similar materials are effective for the removal of these substances from textile fibers. It is necessary, however, in analytical work to use a solvent which has a negligible effect upon the weight of the purified fibers. Carbon tetrachloride meets this requirement.

A portion of the sizing and finishing materials may consist of substances such as starches, gums, casein, and gelatin, which are insoluble in carbon tetrachloride and must be removed by other agents harmless to the fibers. Mixtures of suitable amylolytic and proteolytic enzymes [4] are available for the successful desizing of textiles when the sizing material consists of starches and proteins.

To determine the effect of a desizing treatment consisting of a carbon-tetrachloride extraction followed by a malting or enzyme treatment on the purified fibers, 5-g specimens consisting of approximately equal parts of: (a) purified cellulose-acetate rayon; (b) viscose, nitrocellulose, or cuprammonium rayon; (c) silk; (d) wool; and (e) cotton, or mercerized cotton, were dried for 2 hours at 105 to 110° C, weighed, and extracted for 2 hours with carbon tetrachloride in a

[3] Franz Reinthaler and F. M. Rowe. Artificial Silk, p. 91 (Published (in 1928) by Chapman and Hall, Ltd., London).

[4] 1933 Yearbook of the American Association of Textile Chemists and Colorists. Alphabetical list of Textile Chemical Specialties, p. 318. (Published June 1934 by the Howes Publishing Co., 440 Fourth Ave., New York.)

soxhlet extraction apparatus. The fibers were air-dried, rinsed with warm water, and immersed in a 2-percent enzyme solution [5] at 50° C; the solution was heated to 65 to 70° C and the fibers then kept immersed in the solution for 15 to 30 minutes. The fibers were washed, collected on a bitumen filter, dried, and weighed. The average loss for 10 prepared specimens treated in this manner was less than 0.3 percent of the weight of the fibers, with a maximum loss of 0.4 percent for any of the specimens.

Cellulose-acetate fibers (acetone-soluble type) are readily dissolved by agitating them for 15 minutes in acetone, at room temperature. This treatment has no effect on the weight of the other fibers under consideration and a quantitative separation can readily be effected.

The four remaining kinds of fibers are not so readily separated. However, von Weimarn found that silk [6] and cellulose [7] can be dissolved in a concentrated aqueous solution of calcium thiocyanate. The action of this reagent on cellulose fibers was given further consideration by Williams.[8] McGregor and Fryd [9] were able to separate viscose rayon from cotton in garnetted waste by using an acidified solution of calcium thiocyanate, which boiled at 122 to 123° C. Krais and Markert [10] used a solution of calcium thiocyanate containing 100 g of the "technical" thiocyanate in 100 ml of solution to dissolve one form of regenerated-cellulose rayon (viscose) and silk in the same operation, to separate them from cotton and wool. No attempt is described, however, to separate silk from the regenerated-cellulose rayons with thiocyanate solutions of concentrations that leave rayon fibers, wool, and cotton practically unattacked. Preliminary experiments in the development of a practical method showed that this could be done.

Purified silk fibers were agitated with solutions of calcium thiocyanate of specific gravities 1.1, 1.2, 1.3, 1.4, and 1.5, respectively, at approximately 70° C and the time required to effect a filterable solution was noted. Solutions of thiocyanate of specific gravities 1.1 and 1.5, respectively, required approximately 50 minutes; the intermediate concentrations required from 5 to 10 minutes. When insoluble fibers were present, a longer time was required to dissolve silk. A filterable solution and good separation were always obtained when the fibers were well agitated for 1 hour with calcium-thiocyanate solution of specific gravity 1.20. This had little effect on the other fibers. The silk was dissolved when the solution was neutral or made just acid with acetic acid.

The method of Krais and Markert, referred to above, calls for the separation of viscose and cotton from silk and wool with 80-percent sulphuric acid. This does not appear to be practicable, because silk is about as readily soluble as cotton in the acid. Further, the work already reported [11] shows that sulphuric acid changes the weight of wool.

---

[5] The enzyme mixture used in this work was Degomma D. L., obtained from Röhm & Haas Co., Phila., Pa.
[6] Ind. Eng. Chem. **19**, 109 (1927).
[7] Russ. Chem. Soc. **44**, 772 (1912); Kolloid-Z. **11**, 41 (1912); English translation in Rep. Imp. Ind. Research Inst., Osaka, Japan **4**, no. 7, 17 (1923).
[8] J. Soc. Chem. Ind. **40**, 221T (1921).
[9] J. Textile Inst. **24**, no. 2, T103 (1933).
[10] J. Textile Inst. **23**, P213 (1932).
[11] BS J. Research **12**, 75 (1934) RP635.

The use of calcium-thiocyanate solution for the separation of regenerated-cellulose rayon from cotton and wool was studied. Purified samples of these fibers were prepared for the experiments by cutting the fibers to lengths of about 2 to 4 mm. They were mixed in different combinations and amounts. In one experiment four specimens, each consisting of approximately equal parts by weight of cotton and viscose, were agitated for 45 minutes at 70° C with acidified thiocyanate solutions of concentrations having specific gravities 1.30, 1.33, 1.36, and 1.38. After the treatment the solutions were filtered and the insoluble material was washed, dried, and weighed. Cotton was recovered with less than 0.5 percent change in weight in the experiment using the concentration of specific gravity 1.36 or 1.38, but with the two lower concentrations the residue was found to weigh appreciably more, owing to incomplete solubility and removal of viscose rayon.

As stated above, a solution of specific gravity 1.20 dissolved silk without difficulty. It was found that viscose rayon treated with this solution for 1 hour loses less than 1 percent, and when treated for 2 hours, less than 2 percent of its weight. Although higher concentrations than that of specific gravity 1.36 dissolve rayon, this concentration has the advantage of lower viscosity and is more readily filtered than solutions of higher concentrations. Further experiments showed that solutions of specific gravity 1.35 to 1.36 readily dissolve nitrocellulose, cuprammonium, viscose, and Lilienfeld rayons, and that wool, cotton, or mercerized cotton lose less than 2.5 percent of their weight when treated alone for 2 hours. When treated in the presence of soluble fibers the loss is usually less.

When fibers were treated with calcium-thiocyanate solution under conditions such that they dissolved, they first swelled and gradually formed an apparently homogeneous solution. When the fibers were in tightly twisted yarns, the solution did not have free access to the individual fibers. Some of the fibers swelled and coalesced in a way to protect others from the reagent and several hours were required to obtain a homogeneous solution. The time required for solution was lessened when the fibers were well separated and then agitated while they were dissolving.

The calcium-thiocyanate solutions were prepared from a commercial grade of the salt which was not purified for the purpose except by filtering. To prepare solutions of specific gravities 1.20 and 1.36, respectively, approximately 560 g for a solution of the first concentration and 1,000 g for the second were dissolved in sufficient distilled water to make 1 liter of each. The solutions were made just acid to litmus with acetic acid. Solutions of calcium thiocyanate used for dissolving silk and regenerated-cellulose fibers may be recovered for subsequent use by diluting them with distilled water to produce a solution of specific gravity of 1.1 or less. This precipitates the dissolved silk protein and cellulose, which will settle to the bottom of the container. The clear liquid is then drawn off and evaporated on the steam bath in a large evaporating dish until the desired density is reached. It is filtered just before use. Solutions repeatedly recovered in this way do not appear to have changed in their solvent effect upon fibers.

As previously indicated, adequate means for keeping the fibers in suspension in the solutions must be provided to prevent the formation

of masses of fibers which will dissolve slowly. It has been suggested [12] that the Launder-Ometer [13] be used to provide the agitation. It was tried in this work both with and without monel-metal balls in the jars containing the thiocyanate solution and fibers. The result was incomplete solution of silk and rayon with masses of swollen fibers attached to the bottom and top of the jar and with considerable damage to cotton and wool when metal balls were used to prevent the formation of masses of fibers.

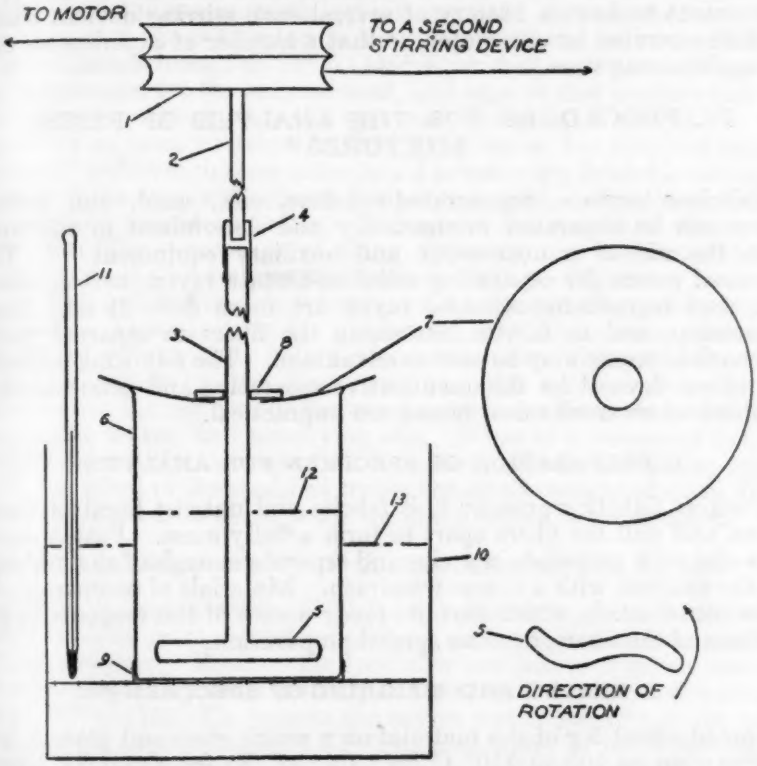

FIGURE 1.—*Mechanical stirring device to furnish mechanical action at a controlled temperature when dissolving silk and regenerated-cellulose rayons.*

1. Double-grooved pulley.
2. Metal shaft.
3. Glass stirring rod.
4. Rubber joint.
5. Glass stirring fins.
6. 600-ml beaker.
7. Watch glass with hole.
8. Rubber washer.
9. Wire-screen support.
10. Container for hot water.
11. Thermometer.
12. Level of thiocyanate solution.
13. Water level.

A simple and convenient apparatus that was used successfully for dissolving fibers in the thiocyanate solution is shown in figure 1. It consists of a water bath for controlling the temperature of the thiocyanate solution within 2° C, a 600-ml beaker with cover, and

[12] See footnote on page 94 of reference 14.
[13] Manufactured by the Atlas Electrical Devices Co., Chicago, Ill.

an inverted T-shaped glass stirrer, which is operated at 320 to 350 rpm. The fins of the stirrer are bent in the direction opposite the direction of rotation to decrease the tendency of the fibers to become wrapped about them. The beaker is held in place by a form made of wire screen and is covered with a watch glass having a hole in the center through which the stem of the stirrer extends. The watch glass should fit the beaker sufficiently well so that not more than 5 ml of water is lost by evaporation from 200 ml of thiocyanate solution in the beaker during the course of agitation for 1 hour at 70° C. It is convenient to have a battery of several such stirring devices which may be operated by one motor, so that a number of experiments can be made at one time.

IV. PROCEDURE FOR THE ANALYSIS OF FIBER MIXTURES[14]

Cellulose acetate, regenerated-cellulose, silk, wool, and cotton fibers can be separated mechanically and determined in mixtures with the aid of a microscope and auxiliary equipment.[15] [16] The chemical means for separating cellulose-acetate rayon, cotton, wool, silk, and regenerated-cellulose rayon are more difficult and time-consuming, and in fabrics containing the fibers in separate yarns mechanical means may be used to advantage. The following methods have been devised for the quantitative separation and determination of fibers where mechanical means are impractical.

1. PREPARATION OF SPECIMEN FOR ANALYSIS

Unravel tightly woven or knit fabrics and untwist highly twisted yarns, and pull the fibers apart to form a fluffy mass. Fasten dense felts and such materials in a vise and separate enough of the material for the analysis with a coarse woodrasp. Materials of comparatively loose construction, which permits ready access of the reagents to the surfaces of the fibers, need no special preparation.

2. DRYING AND WEIGHING OF SPECIMEN[17]

Spread about 5 g of the material on a watch glass and place it in a drying oven at 105 to 110° C (221 to 230° F) for about 1½ hours. Transfer the specimen while warm to a tared weighing bottle, cover the bottle, and place it in a desiccator to cool. Weigh the bottle and contents. Repeat the drying, weighing at intervals of about ½ hour until there is no progressive change in weight of the bottle and contents. All subsequent weighings are made in this manner. Let the weight of the oven-dried specimen be designated *A*.

[14] A tentative procedure for the analysis of fiber mixtures based on our preliminary experiments was submitted to Committee D-13 on Textile Materials of the American Society for Testing Materials on April 12, 1933, at the Committee's request, and was published as Tentative Methods for the Identification of Fibers in Textiles and for the Quantitative Analysis of Textiles, Am. Soc. Testing Materials designation D276-33T. Proc. Am. Soc. Testing Materials **33**, part I, 931(1933).

[15] Edward R. Schwarz, Textiles and the Microscope (published (in 1933), by McGraw-Hill Book Co., Inc., New York).

[16] Paul Heermann und Alois Herzog, Mikroskopische und mechanisch-technische Textiluntersuchungen, 3d ed. (published (in 1931) by Julius Springer, Berlin).

[17] This procedure was followed for all the fibers used in the experiments reported here. A better procedure when analyzing finished textiles of commerce, which may contain substances which harm the fibers or become firmly fixed to them during the drying procedure, is to determine moisture on a sample other than that used for the determination of the different kinds of fibers.

3. DETERMINATION OF TOTAL SIZING, FINISHING, AND OTHER NONFIBROUS MATERIALS

(a) Extract the specimen from (2)[18] in a soxhlet extraction apparatus with carbon tetrachloride for 2 hours. Remove the specimen, allow it to dry, then wash it by agitating it in warm, distilled water, and remove the excess water by squeezing.

(b) Immerse the specimen from (a) in approximately a 0.5-percent solution of a starch and protein-hydrolyzing enzyme at 50° C (122° F), and squeeze the specimen while it is immersed. Repeat the squeezing for at least 6 times to saturate the fibers with the enzyme solution. The solution is heated to 70° C (158° F) or to the temperature known to be optimum for the enzyme used, and kept at this temperature for 15 minutes or more with the specimen immersed in it. Rinse the specimen at least 12 times in fresh portions of hot distilled water, agitate it well in each rinse water to aid in removing insoluble materials such as china clay, and squeeze it after each rinse. Dry the specimen to constant weight as before. This gives the weight of clean, dry fiber, B. The percentage of sizing, finishing, and other nonfibrous materials in the oven-dried specimen, is 100 $(A-B)/A$.

(c) The purpose of this procedure is to remove all nonfibrous constituents. These include the oils, waxes, dirt, and similar materials associated with the fiber before it is processed and sizing and finishing materials added by the manufacturer. The method described is effective for the removal of the usual natural constituents and starch, clay, some waxes, and nondrying oils. When it is necessary for the analyst to modify the procedure to remove certain nonfibrous materials, the effect of the modified treatment on the weight of clean fibers of the same kinds as those in the specimen should be determined.

4. DETERMINATION OF CELLULOSE-ACETATE RAYON

Agitate the specimen from (3) for 15 minutes in about 50 times its weight of acetone at room temperature, and rinse it with two portions of fresh acetone. Remove the specimen and free it of excess acetone by squeezing and permit it to dry. Immerse it in distilled water at about 70° C (158° F), remove the excess water, and dry in the oven as before to constant weight C. The percentage of cellulose-acetate rayon, (acetone-soluble type) in the oven-dried specimen, is 100 $(B-C)/A$.

5. DETERMINATION OF SILK

Cut the residue of fibers remaining from (4) into lengths of about 2 to 4 mm with sharp scissors. Agitate the fibers vigorously for 1 hour at 70° C in 200 ml of a clear solution of calcium thiocyanate of specific gravity 1.20 to 1.21 at 70°±2° C (158° F), made just acid to litmus with acetic acid. Precautions must be taken to prevent evaporation with consequent concentration of the thiocyanate solution during the treatment. Filter the liquid by forming a pad of the insoluble fibers in a small büchner funnel, gooch crucible, or bitumen filter. After a good pad has been formed, combine the portions of the solution, heat it to approximately 70° C and filter it through the pad with the aid of suction. Remove the pad from the filter and agitate it well for 5 minutes in 200 ml of fresh thiocyanate solution at 70° C. Filter,

[18] The numbers in parentheses are citations to determination procedures in section IV.

wash the fibers with hot distilled water until free of thiocyanate, and dry to constant weight D. The percentage of silk in the oven-dried specimen, is 100 $(C-D)/A$.

6. DETERMINATION OF REGENERATED-CELLULOSE RAYON

Pull apart the fibers of the mat left from (5) and if they have been badly felted or twisted together, cut them apart with scissors. Treat the fibers in the same manner as described in (5), but use a solution of calcium thiocyanate of specific gravity 1.35 to 1.36 (at 70° C), made just acid with acetic acid. Obtain the weight E of the dry fibers remaining from this treatment. The percentage of regenerated-cellulose rayon in the oven-dried specimen, is 100 $(D-E)/A$.

7. DETERMINATION OF WOOL PROTEIN

Immerse the specimen from (6) for 10 minutes in a boiling solution of aluminum chloride prepared by dissolving 9 g of the hydrated salt ($AlCl_3.6H_2O$) in 100 ml of water. Remove the specimen from the solution; allow the excess liquid to drain, or lightly squeeze the specimen. Heat it at 105 to 110° C (221 to 230° F), until the cotton has become brown and brittle—2 hours is usually sufficient, but it is often convenient to leave the specimen overnight in an electric oven at this temperature. Immediately on removing the specimen from the oven, place it on a no. 100 sieve, and rub the fibers with sufficient pressure to powder the cellulose and pass it through the screen. Place the wool fibers in a 250-ml beaker and again pass the powdered cellulose through the screen with but little pressure; place the short wool fibers obtained from this second screening operation in the beaker with those of the first and add sufficient hot (70 to 80° C) water to wet them thoroughly. Collect the fibers on a suitable filter as in (5) and agitate them with about 100 times their weight of a solution of hydrochloric acid prepared by diluting 1 part of the concentrated laboratory acid with 9 parts of distilled water. Collect the fibers and wash them with hot distilled water until the wash water gives no test for chlorides with a solution of silver nitrate. Dry to constant weight F. The percentage of wool protein in the oven-dried specimen is 100 F/A, and the percentage of cotton is 100 $(E-F)/A$.

8. ALTERNATIVE METHOD FOR DETERMINATION OF COTTON

Place the specimen from (6) in a boiling 5-percent aqueous solution of potassium hydroxide (previously boiled to remove dissolved air) for 10 minutes; sufficient solution is required to keep the fibers covered during the treatment. Filter the solution, and collect the fibers as a pad. Wash the fibers with hot distilled water, then with 5-percent aqueous solution of acetic acid, and then with distilled water until the wash water is neutral to litmus. Remove the fibers and dry them to constant weight G. The percentage of cotton cellulose in the oven-dried specimen, is 100 G/A.

V. ANALYSIS OF SPECIMENS OF KNOWN COMPOSITION

In order to determine the probable accuracy of the results obtained by the method, portions weighing about 1 g each of the fibers prepared in the manner described in section II were dried to constant weight in an electric drying oven. Specimens of the fibers were subjected to the procedure for removing size and finishing materials described in section IV–3, and then to the treatments prescribed for the separation of the kinds of fibers.

TABLE 1.—*Effect of reagents used to dissolve some fibers on the weight of those considered insoluble*

[Samples 1 to 4 were treated for 1 hour at 70° C with calcium thiocyanate, sp gr 1.20 at 70° C, acidified with acetic acid. Samples 5 to 27 were similarly treated, but thiocyanate of sp gr 1.33 to 1.35 at 70° C was used.]

Sample	Present	Found
VISCOSE		
	Percent	*Percent*
1	100.0	99.0
2	100.0	99.3
3	100.0	99.1
4	100.0	99.4
COTTON		
5	100.0	98.7
6	100.0	98.7
VISCOSE		
11	51.6	51.3
12	49.3	49.9
13	48.3	48.5
14	49.2	49.4
15	48.9	49.0
16	48.7	49.0
17	51.7	52.1
18	50.3	50.6
19	49.8	51.1
VISCOSE (Lilienfeld)		
20	48.6	49.0
21	47.3	47.7
CUPRAMMONIUM		
22	50.8	51.8
23	51.3	52.2
NITROCELLULOSE		
24	50.3	51.2
25	49.4	50.5
26	49.3	49.6
27	50.4	49.8

Sample	Present	Found
MERCERIZED COTTON		
	Percent	*Percent*
7	100.0	97.7
8	100.0	98.2
WOOL		
9	100.0	98.5
10	100.0	99.3
WOOL		
11	48.4	48.7
COTTON		
12	50.7	50.1
13	51.7	51.5
14	50.8	50.6
15	51.1	51.0
16	51.3	51.0
17	48.3	47.9
MERCERIZED COTTON		
18	49.7	49.4
19	50.2	48.9
20	51.4	51.0
21	52.7	52.3
22	49.2	48.2
23	48.7	47.8
24	49.7	48.8
25	50.6	49.5
COTTON		
26	50.7	50.4
27	49.6	50.2

Table 1 shows the effect of the treatments necessary to remove soluble fibers from those considered insoluble when treated by the procedure of section IV. Samples 1 to 4 were treated in the manner specified to dissolve silk, and the results show the loss of weight to be expected when ordinary viscose fibers alone are subjected to this treatment. Samples 5 to 27 were treated to dissolve regenerated-cellulose fibers, and the results show the amount of cotton, mercerized cotton, and wool recovered when treated alone or in mixtures with rayon. Table 2 gives the results of analyses of prepared specimens containing approximately 20 percent each of cellulose-acetate rayon, silk, regenerated-cellulose rayon, mercerized cotton, and wool. Cotton and wool were determined by using a solution of aluminum chloride and heating for removing the cotton, and a boiling solution of potassium hydroxide for removing wool.

TABLE 2.—*Results of analyses of known mixtures of purified cellulose-acetate rayon, silk, regenerated-cellulose rayons, mercerized cotton, and wool fibers*

[Specimens were treated to remove size and finishing materials, then with acetone, acidified calcium thiocyanate of sp gr 1.20, acidified thiocyanate of sp gr 1.35, and aluminum-chloride or potassium-hydroxide solution]

Specimen	Cellulose-acetate rayon		Silk		Regenerated-cellulose rayon (viscose)		Mercerized cotton		Wool	
	Present	Found	Present	Found	Present	Found	Present	Found	Present	Found
	%	%	%	%	%	%	%	%	%	%
1	21.6	21.6	21.3	21.8	19.8	20.3	19.4	[a] 18.2	17.9	18.0
2	20.7	20.7	19.8	20.4	19.2	20.0	19.9	17.9	20.4	[b] 21.1
VISCOSE (LILIENFELD)										
3	19.3	19.2	20.2	20.6	19.5	20.1	21.7	[a] 21.5	19.3	18.6
4	19.8	19.9	21.5	21.8	19.1	20.2	19.6	18.5	19.9	[b] 19.6
CUPRAMMONIUM										
5	21.6	21.3	20.1	20.7	18.7	19.2	20.1	[a] 20.0	19.6	18.9
6	21.2	21.0	20.2	20.7	19.3	20.0	18.9	19.4	20.4	[b] 18.8
NITROCELLULOSE										
7	20.2	20.3	20.3	21.8	20.0	19.4	19.7	[a] 19.4	19.8	19.2
8	20.0	20.0	21.0	22.3	19.0	19.4	19.8	[a] 20.3	19.2	17.8
9	20.1	20.2	20.3	21.0	19.7	20.3	19.9	18.9	19.9	[b] 19.6

[a] Determined by difference, using aluminum-chloride method.
[b] Determined by difference, using potassium-hydroxide method.

The results given in the table show that in a mixture containing cellulose-acetate rayon (acetone-soluble type), silk, regenerated-cellulose rayon as nitrocellulose, viscose, cuprammonium, or Lilienfeld rayons, wool, and cotton or mercerized cotton, the amount of each kind of fiber can be determined by the method within 2 percent of the weight of the specimen analyzed.

WASHINGTON, May 31, 1935.

○